PB86-175999

Supercritical Fluid Extraction of Particulate and Adsorbent Materials

Battelle Pacific Northwest Labs., Richland, WA

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Mar 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-175999

EPA/600/4-86/017

SUPERCRITICAL FLUID EXTRACTION OF PARTICULATE AND ADSORBENT MATERIALS

by

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Interagency Agreement
DW899 30650-01-01
300A02264/TD1880
with U.S. Department of Energy

Project Officer

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ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
RESEARCH TRIANGLE PARK, NC 27711

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/4-86/017	2.
3. RECIPIENT'S ACCESSION NO. PB86 175999/AS	
4. TITLE AND SUBTITLE SUPERCRITICAL FLUID EXTRACTION OF PARTICULATE AND ADSORBENT MATERIALS	5. REPORT DATE March 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Bob W. Wright and Richard D. Smith	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Pacific Northwest Laboratory Richland, WA 99352	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. IAG DW899 30650-01-01
12. SPONSORING AGENCY NAME AND ADDRESS U.S. EPA, Environmental Monitoring Systems Laboratory Methods Development and Analysis Division Methods Development Branch, AMS (MD-44) Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Project 2/84-1/85
	14. SPONSORING AGENCY CODE EPA/600/08
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This report is a summary of work performed by PNL on the extraction of semi-volatile organic materials (SVOCs), for example, polynuclear aromatic compounds, from various adsorbents and environmental matrices, using supercritical fluids (SCFs) as extractants. The results of this work show that supercritical fluids are effective extractants for many SVOCs, and are often competitive with conventional Soxhlet extraction. Advantages of SCFs over conventional methods include higher extraction efficiency, more rapid extraction, and reduced decomposition of thermally labile compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 79
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE $ 11.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Interagency Agreement DW899 30650-01 with the U.S. Department of Energy. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature of processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. Many of these compounds are extremely difficult or impossible to quantify in environmental samples with current analytical methodology. Use of supercritical fluids as extraction solvents and chromatographic eluents has significant potential for extending our methodology to these challenging samples. This report summarizes recent work in development of such supercritical fluid-based analytical methodology.

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ABSTRACT

The applicability of supercritical fluid extraction of semivolatile and heavier molecular weight components from adsorbents and particulate matter was investigated. These studies included off-line supercritical fluid extraction, direct supercritical fluid extraction-mass spectrometry, and on-line supercritical fluid extraction-gas chromatography. A related study on the development of fluorescence detection for capillary supercritical fluid chromatography (SFC) was also conducted.

Gram quantities of spiked XAD-2 resin, SK-4 carbon, polyurethane foam (PUF) plugs, and NBS Urban Dust particles were subjected to off-line extraction, using carbon dioxide, pentane, twenty mole percent methanol in carbon dioxide, and twenty mole percent ethanol in pentane as supercritical fluid extracting solvents under a variety of conditions. The supercritical fluid extractions were more rapid than Soxhlet extractions, but similar extraction efficiencies were obtained. Different extraction recoveries were obtained with the various fluids. Evidence suggests that much better recoveries could be obtained if the collection procedures were modified to eliminate volatilization and aerosol formation after extraction. More rapid extraction procedures also appear feasible.

Direct supercritical fluid extraction-mass spectrometry allowed the extraction profiles for each model compound from the XAD-2 resin to be obtained as a function of time. The compounds displayed different threshold pressures at which extractability was detected and widely varying decay curves as the material was removed.

To develop methods to eliminate or minimize sample preparation procedures, studies using on-line supercritical fluid extraction-gas chromatography were conducted. With this methodology, milligram quantities of samples such as particles or adsorbents were selectively extracted using supercritical carbon dioxide at various pressures followed by capillary gas chromatographic analysis of each extract. The technique was applied to the NBS Urban Dust particles to demonstrate that selective and direct analyses could be obtained.

To obtain high detection sensitivity for SFC using fluids that are incompatible with flame ionization detection, development of reliable capillary SFC fluorescence detection was also undertaken. The necessary modifications of a commercial HPLC fluorescence detector were completed and successfully interfaced to an SFC instrument using supercritical pentane as a mobile phase. The model compounds from the extraction studies were used to demonstrate successful chromatographic separation and fluorescence detection.

This report was submitted in fulfillment of Interagency Agreement DW899 30650-01 by Pacific Northwest Laboratory under the sponsorship of the U.S. Environmental Protection Agency through a Related Services Contract with the U.S. Department of Energy under Contract DE-AC06-76RLO-1830. This report covers a period from February 1, 1984 to January 31, 1985, and work was completed as of January 31, 1985.

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SECTION 1

INTRODUCTION

Numerous methods and combinations of methods with varying degrees of complexity are currently employed to prepare samples for analysis. Less complex, more rapid, and more sensitive preparation procedures would be desirable in many cases, particularly for small samples or low concentrations of analytes. Supercritical fluid extraction procedures are attracting attention for use in selective large-scale process applications (1), but only limited attention has been given to using supercritical fluid extraction methods in analytical applications. The goals of this study were to determine the potential utility of supercritical fluid extraction for analytical sample preparation and to develop improved methods of analysis utilizing these procedures.

The potential advantages of supercritical fluid extraction accrue from the properties of a solvent at temperatures and pressures above its critical point. At elevated pressure this single phase will have properties which are intermediate between those of the gas and liquid phases and are dependent upon the fluid composition, temperature, and pressure. The compressibility of supercritical fluids is large just above the critical temperature; at this point small changes in pressure result in large changes in the density of the fluid (2). Figure 1 shows a typical pressure-density relationship in terms of reduced parameters (e.g. pressure, temperature, or density divided by their respective critical parameter). Isotherms for various reduced temperatures show the variations in density which can be expected with changes in pressure. Thus, the density of a supercritical fluid will be typically 10^2 to 10^3 times greater than that of the gas. Consequently, molecular interactions increase due to the shorter intermolecular distances. However, the diffusion coefficients and viscosity of the fluid remain similar to that of the gas. The "liquid-like" behavior of a supercritical fluid results in greatly enhanced

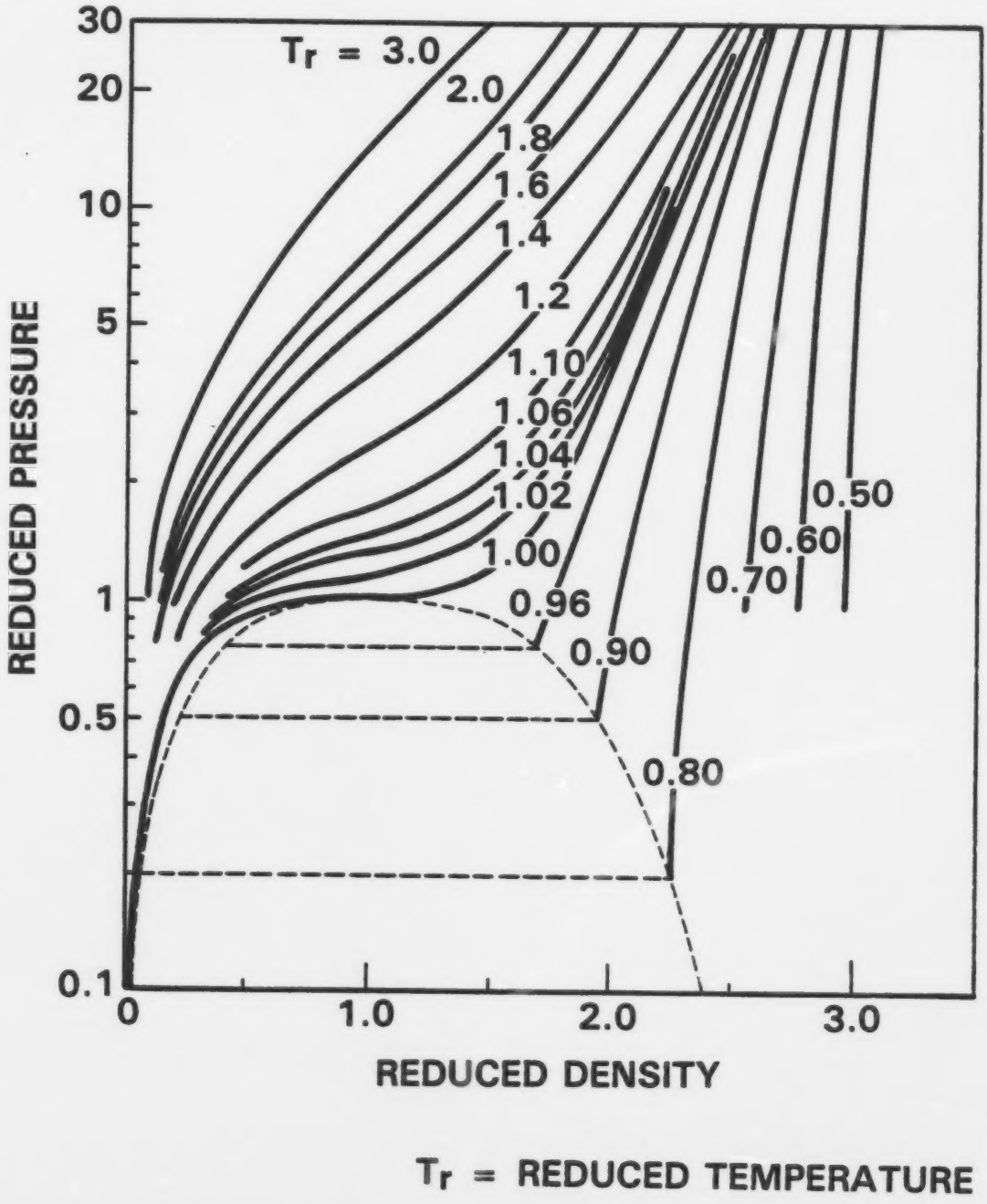

Figure 1. Typical pressure-density behavior of a pure supercritical fluid.

solubilizing capabilities compared to a subcritical gas, but with higher diffusion coefficients, lower viscosity, and an extended temperature range compared to the corresponding liquid. These properties allow similar solvent strength and the potential for more rapid extraction rates than possible with liquids.

This report describes various studies conducted to evaluate the applicability and efficiency of analytical supercritical fluid extraction methods. These investigations were among the very first to specifically address the use of supercritical fluid extraction for analytical purposes. Consequently, little related information exists. The studies involved in this project included off-line supercritical fluid extraction of adsorbents and particles, direct supercritical fluid extraction-mass spectrometry, and on-line supercritical fluid extraction-gas chromatography. A fluorescence detection supercritical fluid chromatography (SFC) system was also developed. Gram quantities of XAD-2 resin, SK-4 carbon and polyurethane foam (PUF) were spiked with selected large polycyclic aromatic compounds and subjected to supercritical fluid extraction using either carbon dioxide, a carbon dioxide-methanol mixture, pentane, or a pentane-ethanol mixture as extracting fluids. NBS Urban Dust (SRM 1649) was also subjected to the same extraction conditions. The extraction efficiency as a function of the extracting fluid was evaluated. Traditional liquid Soxhlet extractions of the same matrices were conducted and compared to the supercritical fluid extractions. Preliminary extractions using direct supercritical fluid extraction-mass spectrometry were also conducted to obtain individual extraction profiles as a function of time for each of the spiked compounds. Direct analysis methods, in which sample preparation and analysis are combined, were investigated using on-line supercritical fluid extraction-gas chromatography with the NBS Urban Dust as a sample matrix. Fluorescence SFC detection was developed to provide high detection sensitivity using supercritical fluid systems that are not compatible with flame ionization detection.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn as a result of the off-line supercritical fluid extraction studies:

- High molecular weight polycyclic aromatic compounds at ppm concentrations can be extracted from typical adsorbent matrices using supercritical fluid extraction methods. The various fluids displayed different extraction strengths, with carbon dioxide generally being poor and the alcohol-modified mixtures good extracting fluid systems.
- Supercritical fluid extraction provided relatively fast extractions (1-2 hrs or less) compared to traditional Soxhlet extraction.
- Of the fluids studied, the carbon dioxide-methanol mixture and pentane fluid systems gave the best extraction recoveries from the XAD resin. Carbon dioxide at 50°C was a poor extraction solvent. Under the experimental conditions used, Soxhlet extraction with methylene chloride gave higher extraction recoveries than the supercritical fluid extractions.
- All supercritical fluid and Soxhlet extractions gave poor recoveries from the activated carbon. The pentane-ethanol fluid system gave the best overall results. Soxhlet extraction after supercritical fluid extraction gave higher extraction recoveries than Soxhlet extraction before supercritical fluid extraction.
- The PUF matrix was soluble in the supercritical fluids. Even so, after appropriate clean-up of the extracts, comparable or higher extraction efficiencies were achieved with both carbon dioxide-methanol and pentane fluid systems as compared to Soxhlet extraction with

methylene chloride. Carbon dioxide at 50°C was a poor extraction solvent.

- The pentane-ethanol fluid system gave the highest recovery of material with the best extraction efficiency from the Urban Dust. Carbon dioxide at 50°C and pentane at 210°C gave poor extraction recoveries. Additional material was extracted by Soxhlet extraction with methylene chloride following supercritical fluid extraction.
- In most cases higher extraction efficiencies (recoveries) were obtained with Soxhlet extraction than with supercritical fluid extraction. However, it appears there was a problem with the collection of the supercritical fluid extracts, and a large percentage of material was lost due to aerosol formation. Unfortunately, this problem was not discovered until after completion of the work discussed above. Preliminary results using a collection system in which the total extraction effluent was trapped by freezing in a sealed vessel cooled in liquid nitrogen indicate that comparable extraction efficiencies can be obtained with both supercritical fluid and Soxhlet extractions.

The following other conclusions can be drawn from the remainder of the studies in this project:

- Direct supercritical fluid extraction-mass spectrometry provides a valuable means of simultaneously monitoring the extraction kinetics and threshold pressures for a number of compounds. An understanding of these parameters is necessary to obtain selective fractionation of complex samples.
- On-line supercritical fluid extraction-gas chromatography provides a means of eliminating sample preparation and allows automated extraction and analysis of organic matrices. By utilizing the variable solvating power of supercritical fluids, selective extractions were demonstrated.
- Highly sensitive fluorescence detection for capillary supercritical fluid chromatography was developed for use with fluid systems that are incompatible with flame ionization detection.

Recommendations for resolving problems and expanding similar research areas are listed below:

- The off-line supercritical fluid extraction studies should be repeated using the improved collection system (e.g. freezing of the extraction effluent in a sealed flask cooled in liquid nitrogen) to prevent recovery losses. These results would be more meaningful than the existing data in terms of comparing extraction efficiencies between the various fluid systems and to Soxhlet extractions.
- Spiked adsorbents and particulate samples should be subjected to supercritical fluid extraction after Soxhlet extraction to determine if additional material can be recovered.
- Larger volumes of the supercritical extraction fluids (> 250 mL liquid volume) should be utilized to determine if more complete extraction can be obtained.
- Methods of enhancing extractabiiity by recycling the fluid or improving fluid contact with the sample matrix should be investigated.
- Combined extraction-fractionation procedures in which a series of successive depressurization steps are utilized to collect discrete solubility fractions from the matrix should be investigated.
- Work on direct supercritical fluid extraction-mass spectrometry should be continued using isobaric conditions to obtain extraction kinetics data. These data would be useful for defining the optimum conditions to selectively extract specific compounds from a complex matrix.
- The on-line supercritical fluid extraction-gas chromatography methodology should be applied to additional sample matrices, and investigations should be conducted to answer questions concerning quantitative methods. Extraction kinetics could also be studied using the instrumentation.
- The fluorescence detection supercritical fluid chromatography instrumentation should be evaluated for quantitative analysis and applied to the nonvolatile materials in the model compound mixture.

SECTION 3

MATERIALS AND METHODS

ADSORBENTS AND PARTICLES

The following materials were chosen as adsorbents for the extraction studies: purified XAD-2 resin, 20/60 mesh (Alltech, Deerfield, IL), polyurethane foam plugs (General Metal Works, Cleves, OH), and SK-4 carbon, 100/120 mesh (Alltech, Deerfield, IL). A National Bureau of Standards air particle sample, Urban Dust SRM 1649, was used for particle extraction.

Adsorbent Pretreatments

The adsorbents were cleaned and equilibrated at two humidity levels prior to spiking with the model compounds. Purified XAD-2 resin was purchased that had been cleaned and evaluated by an EPA procedure established for the preparation of resins free of extractable organics (EPA-600/7-78-201). The polyurethane foam plugs (PUF) were cleaned using a procedure developed for the Methods Development Branch of the EPA. This procedure involved squeezing the PUF cartridges in two solvents. The PUF cartridges were first placed in toluene and squeezed ten times by using the base of a graduated cylinder. The process was repeated using acetone followed by drying in a nitrogen stream. The SK-4 carbon was cleaned by Soxhlet extraction in carbon disulfide for sixteen hours followed by baking at 100°C for several hours.

The adsorbents were equilibrated in controlled humidity atmospheres by storing the cleaned materials in large desiccators. The adsorbents were placed in shallow dishes to allow maximum exposure and diffusion. Approximately an eighty percent relative humidity atmosphere was generated by placing a saturated aqueous solution of ammonium chloride in the closed desiccator (3). A dry (< ten percent relative humidity) atmosphere was obtained by placing freshly dried desiccant (anhydrous calcium chloride and sodium sulfate) in

the closed container. The desiccators were maintained at room temperature (~ 23°C).

MODEL COMPOUNDS

The model compounds were chosen from the higher molecular weight polycyclic aromatic compounds to cover a range of volatility and polarity. The compounds included chrysene (mw = 228), coronene (mw = 300), decacyclene (mw = 450), rubrene (mw = 532), benzanthrone (mw = 230), 1-nitropyrene (mw = 247), 6-aminochrysene (mw = 243), and dibenzo(a,i)carbazole (mw = 267). A standard solution containing each of the compounds at an approximate concentration of 100 ng/µL in benzene was prepared. The solution was refrigerated and stored in the dark until used.

Adsorbent Spiking

The adsorbents were spiked by injecting a liquid aliquot of the model compound solution onto the surface of the adsorbents and allowing the solvent to air evaporate. Approximately one gram quantities of the XAD-2 resin and the SK-4 carbon were loaded into 5.4 x 1.3 cm o.d. borosilicate glass extraction tubes and spiked at 5 and 50 ppm by injecting 50 µl and 500 µl, respectively, of the model compound standard solution per piece. The PUF plugs were cut into 0.5 gram pieces and spiked at the same levels using 25 µl and 250 µl volumes of the standard solution. The solvent was allowed to evaporate from the adsorbents prior to extraction. Approximately two gram quantities of the Urban Dust were used for the particle extractions.

FLUIDS AND SOLVENTS

Anaerobic grade carbon dioxide (Airco) was used for the extracting fluid. All solvents used to prepare fluid mixtures (i.e., methanol, pentane, and absolute ethanol) were high purity pesticide grade or better (Burdick and Jackson or equivalent). Solvents used for Soxhlet extraction and sample preparation (methylene chloride, methanol, carbon disulfide and benzene) were also high purity pesticide grade or better (Burdick and Jackson or equivalent).

SECTION 4

EXPERIMENTAL PROCEDURES

OFF-LINE SUPERCRITICAL FLUID EXTRACTION

The adsorbent materials that had been spiked with the model compounds and the air particle sample were subjected to off-line supercritical fluid extraction using carbon dioxide, pentane, a carbon dioxide-methanol mixture (20 mole % methanol), and a pentane-ethanol mixture (20 mole % ethanol).

Apparatus

A schematic diagram of the supercritical fluid extraction system is shown in Figure 2. A modified Varian 8500 syringe pump (250 mL capacity) was used to pressurize and deliver the supercritical fluid extraction solvents. The pump was modified to allow pressure programming and operation in a pressure limiting mode. The pressurized fluid was transferred to the 316 stainless steel high-pressure extraction vessel (see detail and design of extraction vessel in Figure 3) through 1/16 inch stainless steel tubing. The extraction vessel was maintained at elevated temperatures in a Hewlett-Packard 7625A gas chromatograph oven. The tubing from the syringe pump extended to the bottom of the extraction cell chamber, where the sample was placed in a 5.4 x 1.3 cm o.d. borosilicate glass test tube for easy placement and removal. This allowed the extraction fluid to move through the sample from bottom to top and then exit the extraction vessel. A stainless steel frit (2.0 - 5.0 μm pore size) was placed in the exit port of the extraction vessel to prevent any sample material from being flushed out. The 1/16 inch tubing carrying the extract stream was maintained in a heated transfer line after exiting the oven. It was then connected to a length (approximately 10-12 cm) of 50 μm i.d. stainless steel tubing, which was crimped on the exit end to control the flow and serve as a depressurization zone for the extraction effluent. The extracts

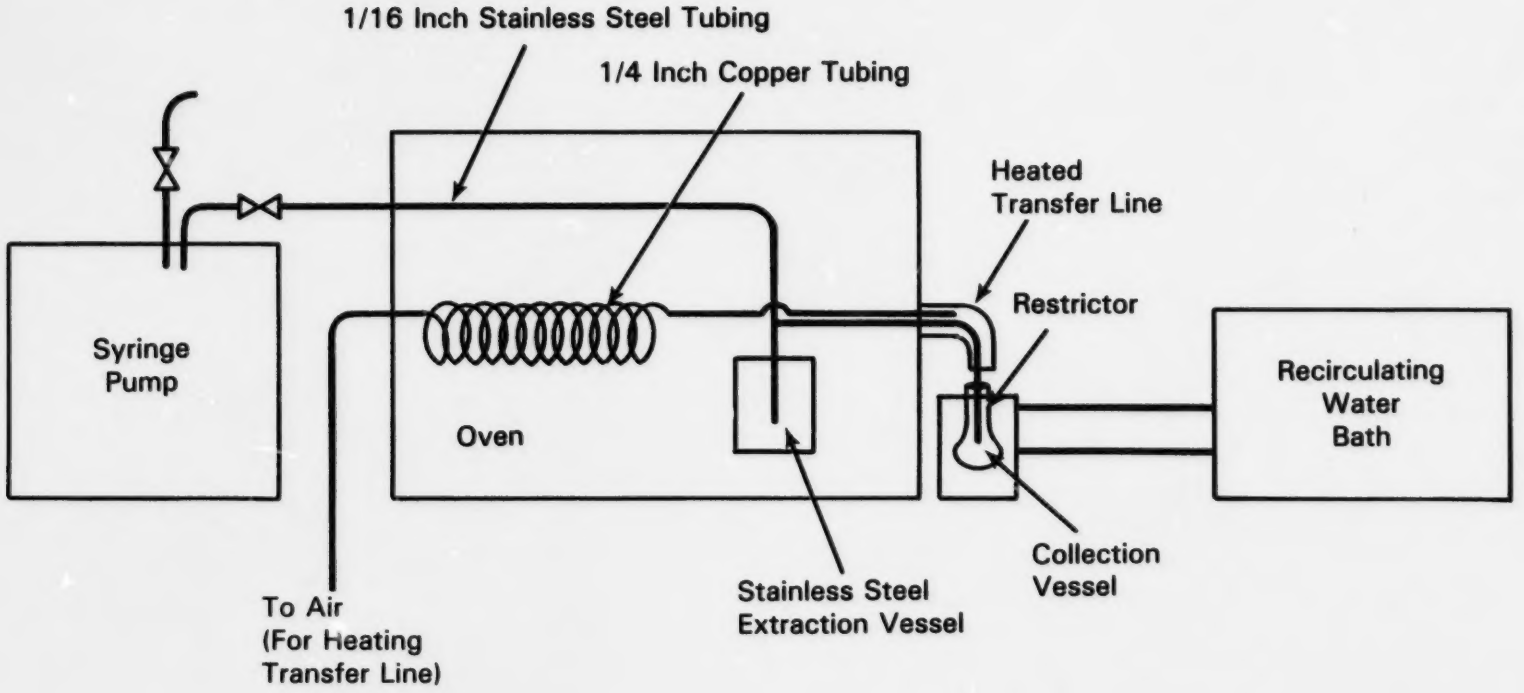

Figure 2. Schematic diagram of the supercritical fluid extraction apparatus.

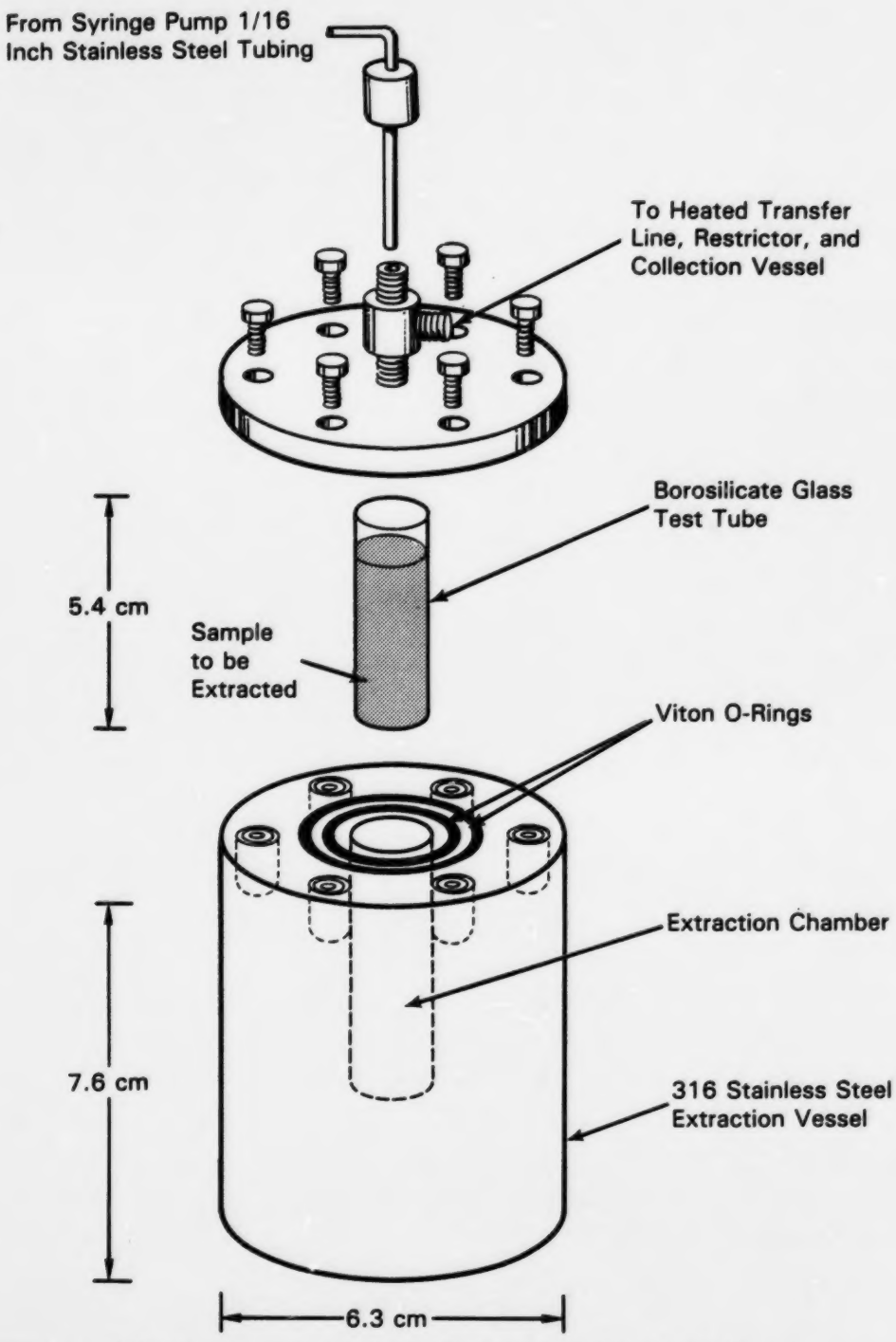

Figure 3. Detail of supercritical fluid extraction vessel.

were collected in volumetric flasks that were cooled to ~ 0°C with a recirculating water/antifreeze bath (Brinkman RC 3). In later work, selected carbon dioxide extracts were collected by freezing the effluent in a sealed round bottom flask cooled in liquid nitrogen. After extraction, the carbon dioxide was allowed to thaw, leaving the extract behind. The restrictor was heated and maintained at the desired temperature by applying an electrical current as shown in Figure 4.

CO_2 Extractions

Each individual extraction tube containing the weighed and spiked adsorbents or particles was sealed inside the extraction vessel. The extraction vessel was placed in the oven and connected to the appropriate transfer lines. Extraction temperatures were 50°C and 150°C. The transfer line region was adjusted to approximately the same temperature as the oven. Air heated in the oven and forced into the transfer line region provided additional heating control. The syringe pump was filled with 250 mL of liquid carbon dioxide. The extracting fluid was delivered to the extraction vessel by pressure programming from 70 to 410 atmospheres at 10 atmospheres/min. The extraction was allowed to continue at the upper pressure until the fluid supply was exhausted. The restrictor was maintained at temperatures between 40°C and 80°C.

CO_2-Methanol Extractions

The particles and spiked adsorbents were also subjected to extraction using a mixed carbon dioxide-methanol solvent system. An approximately 20 mole percent methanol in carbon dioxide mixture was prepared by loading 59 mL of methanol into the syringe pump and then filling the remaining 191 mL with liquid carbon dioxide. An extraction temperature of 150°C with a similar transfer line temperature was utilized. No external heat was applied to the restrictor. The extracting fluid pressure was programmed from 75 to 410 atmospheres at 10 atmospheres/min and held at the upper pressure for the duration of the pump volume. The flow rate typically ranged between 1.5 and 2.5 mL/min liquid volume. After extraction, the collected methanol was heated slightly (~ 60°C) and evaporated under a nitrogen purge.

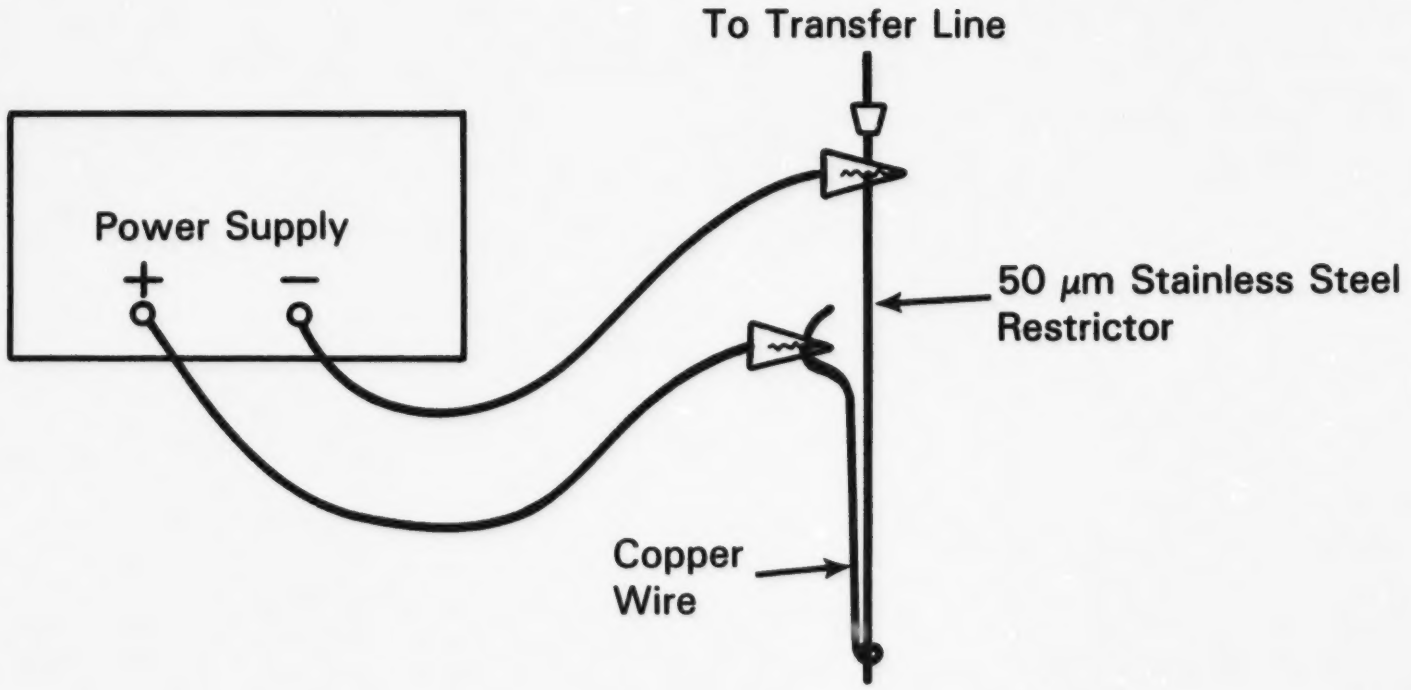

Figure 4. Schematic diagram of heated restrictor assembly.

Pentane Extractions

A supercritical pentane fluid was also used to extract the adsorbents and particles. The extraction was performed at 210°C, and the transfer line region was maintained at a similar temperature. No external heat was applied to the restrictor. The pentane was pressure-programmed from 30 to 165 atmospheres at 10 atmospheres/min and held at the upper pressure until the 250 mL pump volume was exhausted. After completion of the extraction it was necessary to evaporate the collected pentane from the sample extract. This was done with a nitrogen purge at room temperature to minimize any sample loss due to volatilization.

Pentane-Ethanol Extractions

An approximately 20 mole percent mixture of ethanol in pentane was also used as an extraction fluid for the particles and adsorbents. The fluid mixture was prepared by mixing 12.7 volume percent of absolute ethanol in pentane. An extraction temperature of 215°C and a pressure program of 30 to 165 atmospheres at 10 atmospheres/min was utilized for this fluid. A 250 mL syringe pump volume was used. No external heat was applied to the restrictor. The collected pentane-ethanol extract mixture was evaporated following completion of the extraction. It was necessary to raise the temperature to approximately 60°C to remove the ethanol with the nitrogen purge.

Soxhlet Extractions

All supercritical fluid-extracted samples were also subjected to Soxhlet extraction. Some samples were Soxhlet extracted only to provide a comparison between the techniques. Soxhlet extractions were accomplished using acid-washed glassware and pre-extracted thimbles. Approximately 200 mL of methylene chloride was used as the extraction solvent. Extractions were conducted for 16-18 hours with a cycle time between 15 and 20 minutes. In some instances, methanol was also used as an extraction solvent.

Gas Chromatography

Capillary gas chromatography (GC) was used to quantify the material recovered from the supercritical fluid and Soxhlet extractions. A Hewlett-Packard 5880 gas chromatograph equipped with a capillary injection system,

flame ionization detector, and an autosampler was used for these analyses. A 15 m x 0.25 mm fused silica column coated with SE-54 stationary phase was installed in the chromatograph. Hydrogen at a linear velocity of 100 cm/sec was used for the carrier gas to expedite elution of the heavier molecular weight compounds. A temperature program starting at 50°C and ramped to 180°C at 10°C/min followed by a ramp of 4°C/min to 300°C was generally used to elute the components. Quantification was achieved using an internal standard method with external calibration. Response factors were calculated from three concentration levels of standards (prepared from the standard solution used to spike the adsorbents) bracketing the concentration range of the analytes. 2-chloroanthracene at a level of 50 ng/µl was used as internal standard.

DIRECT SUPERCRITICAL FLUID EXTRACTION-MASS SPECTROMETRY

Initial experiments using mass spectrometric monitoring of the extraction stream were conducted using supercritical carbon dioxide and approximately one-gram of XAD-2 resin spiked at 50 ppm with the model compounds.

Apparatus and Conditions

The instrumentation used for the direct supercritical fluid extraction-mass spectrometry (SFE-MS) is similar to that previously described (4,5). A schematic illustration of the instrumentation is shown in Figure 5. High pressure carbon dioxide was generated using a Varian 8500 syringe pump. The pump was modified to operate under computer or microprocesser control to allow pressure programming capability. For this extraction the pressure was ramped from 72 to 400 atmospheres at 20 atmospheres/minute. A Hewlett-Packard 5790 gas chromatograph oven provided constant temperature conditions (150°C) for the extraction vessel and heated air used to control the temperature of the mass spectrometer interface probe. The same extraction vessel as used for the off-line extractions described in the previous section was used for these studies. The effluent from the extraction cell was transported to the ion source through 50 µm i.d. fused silica tubing. A short length (1-3 cm) of 5 µm i.d. fused silica tubing served as a depressurization zone to form the interface between the supercritical fluid and the vacuum in the mass spectrometer. The effluent was injected axially in the chemical ionization (CI) source

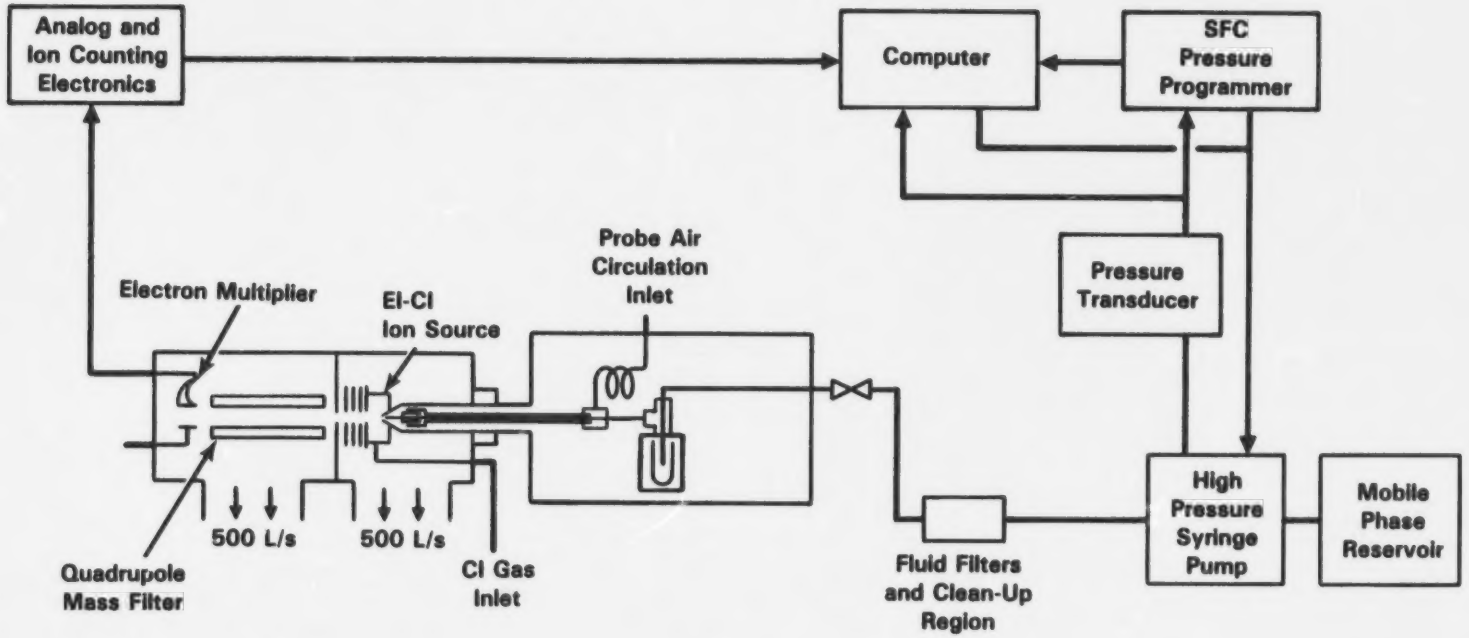

Figure 5. Schematic diagram of the supercritical fluid extraction-mass spectrometry instrumentation.

of an Extranuclear quadrupole mass spectrometer. Methane was used for the CI reagent gas and was adjusted to provide optimum CI conditions. The mass spectrometer was set to scan the expected $(M+1)^+$ ions for each of the model compounds. The extraction was operated for 210 minutes during which time mass spectral data were continuously stored and several milliliters of the liquid carbon dioxide spent.

ON-LINE SUPERCRITICAL FLUID EXTRACTION-GAS CHROMATOGRAPHY

The Urban Dust particles and other samples were also subjected to on-line supercritical fluid extraction-gas chromatography analysis. The particles were extracted at various pressures using supercritical carbon dioxide. The extraction effluent was decompressed in the inlet of a capillary gas chromatography column to deposit the solvated compounds. Regular temperature-programmed capillary gas chromatographic analyses were then performed.

Apparatus

A schematic diagram of the on-line supercritical fluid extraction-gas chromatography instrumentation is shown in Figure 6. A computer-controlled Varian 8500 syringe pump provided a high pressure supply of carbon dioxide. The sample was placed in a small volume extraction cell (~ 50 µl) equipped with frits (0.5 µm pore size) on each end to contain the sample material. The extraction cell was placed inside a heated block to control the extraction temperature. An air-actuated Rheodyne 7010 six-port switching valve was used to direct the extraction cell effluent either to the analytical column for on-column deposition of the extract or to a collection reservoir. Short lengths (1-3 cm) of small internal diameter (5-7 µm) fused silica were used as pressure restrictors to maintain supercritical pressures up to the point of deposition or collection. The restrictor for the on-column deposition was mounted through a tee to allow the gas chromatograph carrier gas to enter coaxially along the restrictor. This region was also mounted in a heated block to control the temperature of the restrictor and expansion region. After deposition of the extract into the analytical column was completed (and the effluent switched to the vent position for collection), high pressure carrier gas was connected to the on-column restrictor to purge any remaining

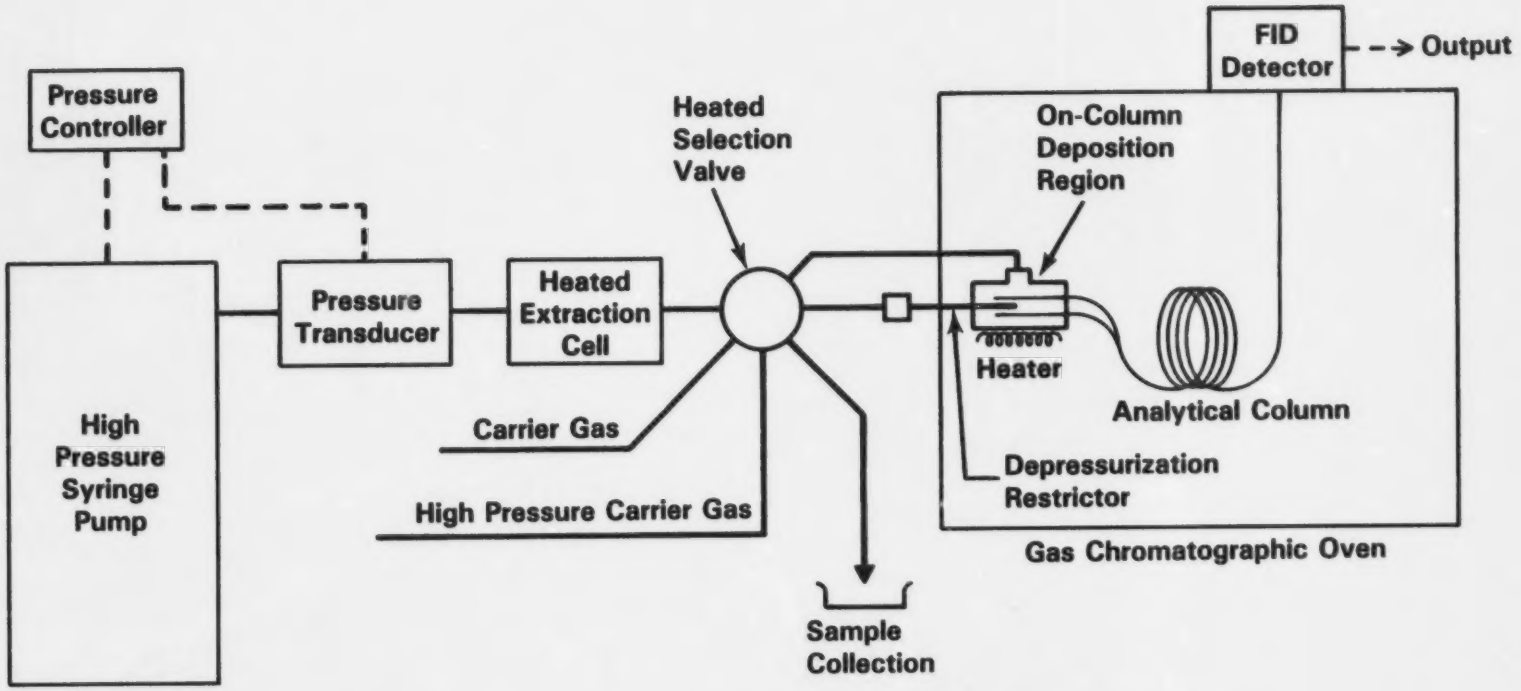

Figure 6. Schematic diagram of the on-line supercritical fluid extraction-gas chromatography instrumentation.

material into the analytical column. After the purging process was complete, the gas chromatograph was temperature-programmed to complete the analysis. Typically, 15m x 0.25 mm fused silica capillary columns coated with a standard film thickness (0.25 μm) of crosslinked SE-54 (5% phenyl polymethylphenylsiloxane) stationary phase were used for analytical columns. The gas chromatograph was equipped with a flame ionization detector.

Automated Extractions

A few milligrams of the sample (e.g. Urban Dust) were loaded in the extraction cell. The extraction cell and the switching valve were typically heated to between 40° and 50°C. The restrictor heating block was maintained at approximately 275°C. The system was automated to allow selective extractions by extracting at different pressures and analyzing the extract each time. Typically, extractions would be started at lower pressures and then progressively increased for each additional extraction. The extractions were usually started at pressures near the critical point (73 atm) of carbon dioxide with the effluent being collected on-column for 3-10 minutes. The effluent would then be vented, while a high pressure carrier gas purged the restrictor for an additional 3-10 minutes. Temperature-programmed GC analyses starting near ambient conditions and ramped between 4° and 8°C/min to an upper temperature of 250° -300°C were typically performed. After a GC analysis was completed, the supercritical fluid extraction pressure would be increased and another analysis performed.

FLUORESCENCE DETECTION SUPERCRITICAL FLUID CHROMATOGRAPHY

To obtain high detection sensitivity with fluid systems that are incompatible with flame ionization detection, a fluorescence detection method for capillary supercritical fluid chromatography (SFC) was developed.

Apparatus

Essentially the same instrumentation as used for flame ionization SFC (6,7) was modified for fluorescence detection. The high pressure fluid supply (usually pentane) was controlled and delivered by a Brownlee MPLC pump. The pump was operated in the SFC mode which allowed pressure-controlled operation and pressure programming capability. A Hewlett-Packard 5840 gas chromato-

graph oven was used to provide constant temperature conditions. A Valco C14W HPLC valve with a 60 nl volume rotor was used for sample introduction. The injection valve was maintained at ambient temperatures and was connected to the chromatographic column through a splitter. The splitter was adjusted to allow approximately a 1:3 to 1:10 flow in the chromatographic column. The chromatographic columns were typically 5-15 m lengths of 50 μm i.d. fused silica that were deactivated and coated with an extensively crosslinked (8) polysiloxane stationary phase (e.g. 5% or 50% phenyl polymethylphenylsiloxane, SE-54 or OV-17 gum, respectively).

Detection was accomplished using a modified Schoeffel Instrument FS 970 HPLC fluorescence detector. The flow cell was removed and replaced with a length of 250 μm i.d. fused silica with a small window formed by burning off 3-4 mm of the polyimide coating. The analytical column (210 μm o.d.) was threaded through the larger tubing and extended to a point immediately below the window. The larger window tubing and the analytical column were connected with a Supelco butt-connector. Decompression of the supercritical fluid mobile phase and flow rate regulation were accomplished by connecting a short length of restrictor tubing to the exit end of the window tubing. Consequently, detection was accomplished prior to decompression, but since the detector region was unheated, the fluid had returned to the liquid phase. The small window on the 250 μm i.d. tubing was carefully aligned in the light path of the tungsten lamp. Appropriate slits were used to illuminate only the interior of the cell to minimize the background from any diffracted light. A schematic diagram detailing the modified 2π steradian fluorescence collection system and on-column flow cell is shown in Figure 7.

Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) with fluorescence detection was applied to the model compound mixture. Pentane at a temperature of 210°C was used as the mobile phase. Typical pressure programs ranged from 410 (slightly subcritical) to 800 psig at ramp rates of 10-20 psi/min. In general, the pressure was held at the lower level until after elution of the solvent peak. The pressure was ramped down slowly between chromatographic runs to prevent damage to the stationary phase from too rapid decompression. The linear

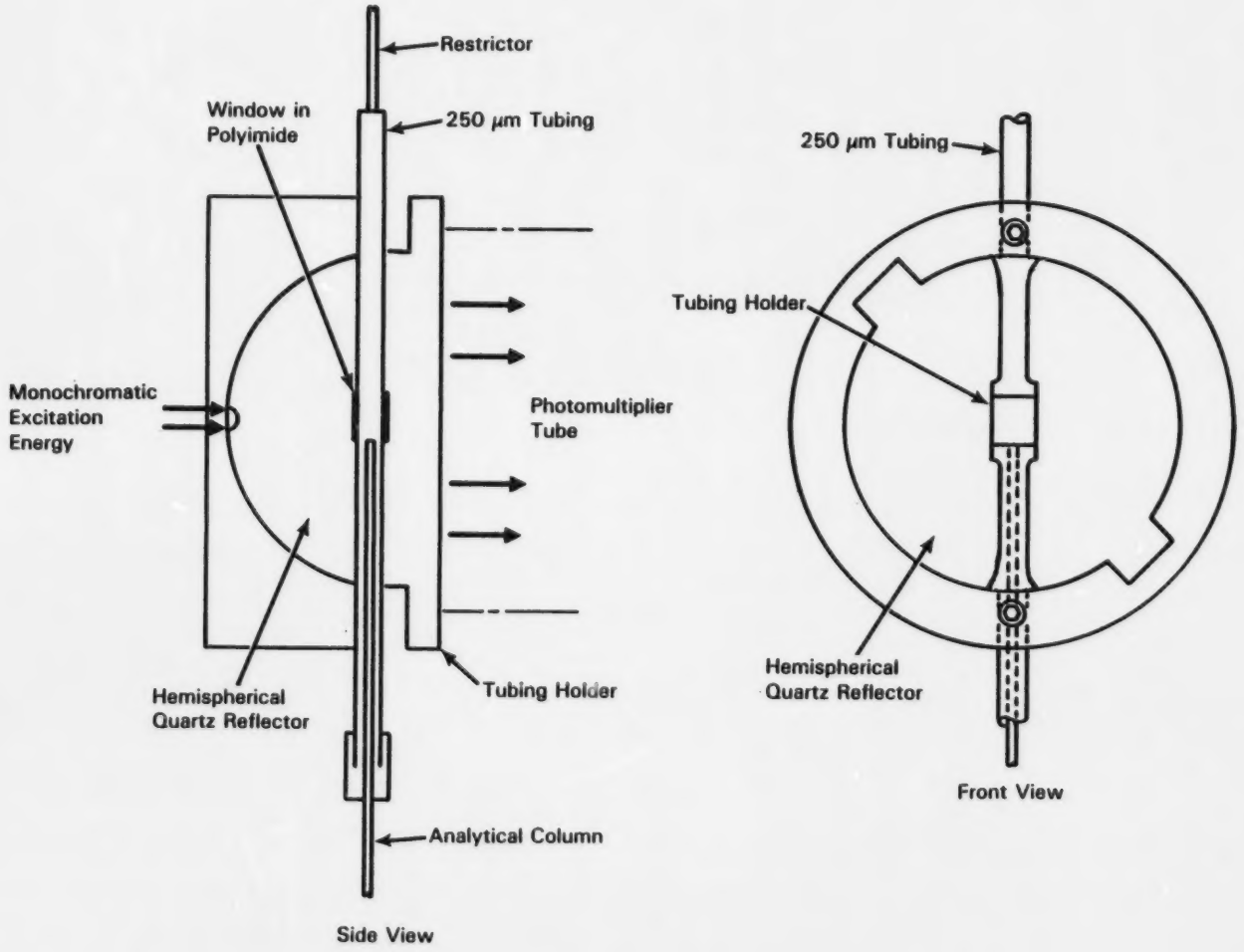

Figure 7. Schematic diagram of on-column fluorescence detection system.

velocity of the mobile phase was adjusted between 1.5 and 3.5 cm/sec. An excitation wavelength of 254 nm was usually chosen, but other excitation wavelengths were also used. To maintain maximum sensitivity no emission filters were typically used. The photomultiplier was operated at voltages as high as possible without generating excessive noise (~ 425V).

SECTION 5

RESULTS AND DISCUSSION

OFF-LINE SUPERCRITICAL FLUID EXTRACTION

A summary of the supercritical fluid extraction parameters used for the spiked XAD-2 resin, SK-4 carbon and PUF adsorbents is given in Table 1. Critical temperatures and pressures as well as the extraction temperatures and pressures are given for each of the four fluid systems employed. The results of the off-line supercritical fluid extraction of adsorbents and particles will be given in the following order: XAD-2 resin, SK-4 activated carbon, PUF, and NBS Urban Dust. Following the discussions of the adsorbent and particulate matter extractions, the effects of an improved collection method utilizing a liquid nitrogen cooled flask will be presented.

Capillary GC quantitative results will be given for each of the individual spiked components extracted from the various adsorbents by supercritical fluid extraction, Soxhlet extraction, and Soxhlet extraction after supercritical fluid extraction. The amount of each component which was spiked onto and recovered from the adsorbents will be given in parts per million (ppm; µg/g) along with the calculated percent recovery. 50 ppm spikes onto 10% humidity-equilibrated adsorbents were extracted with the supercritical fluids; 50 and 5 ppm spikes onto 10 and 80% humidity-equilibrated adsorbents were Soxhlet-extracted. The results presented will allow both the extraction efficiencies of various supercritical fluids to be compared and supercritical fluid and Soxhlet extraction methods to be compared.

XAD-2 Resin

Capillary gas chromatograms are shown in Figure 8 for the CO_2-methanol supercritical fluid extract and the subsequent Soxhlet extract of the spiked XAD-2 resin adsorbent. Six of the eight spiked components are labeled and

TABLE 1. SUMMARY OF SUPERCRITICAL FLUID EXTRACTION PARAMETERS

Fluid	Critical Temperature (°C)	Critical Pressure (atm)	Extraction Conditions			
			Temperature (°C)	Pressure (atm)	Reduced Temperature	Reduced Pressure
CO_2	31.1	73.0	50	410	1.06	5.62
			150	410	1.39	5.62
CO_2-methanol[a]	120[b]	167[b]	150	410	1.08	2.46
Pentane	197.2	33.0	210	165	1.03	5.00
Pentane-ethanol[c]	~205[d]	~38[d]	215	165	1.02	4.34

a 20 mole percent methanol in carbon dioxide.
b Ref. 9.
c 20 mole percent ethanol in pentane.
d Calculated using binary mixture critical point estimation methods, Ref. 10.

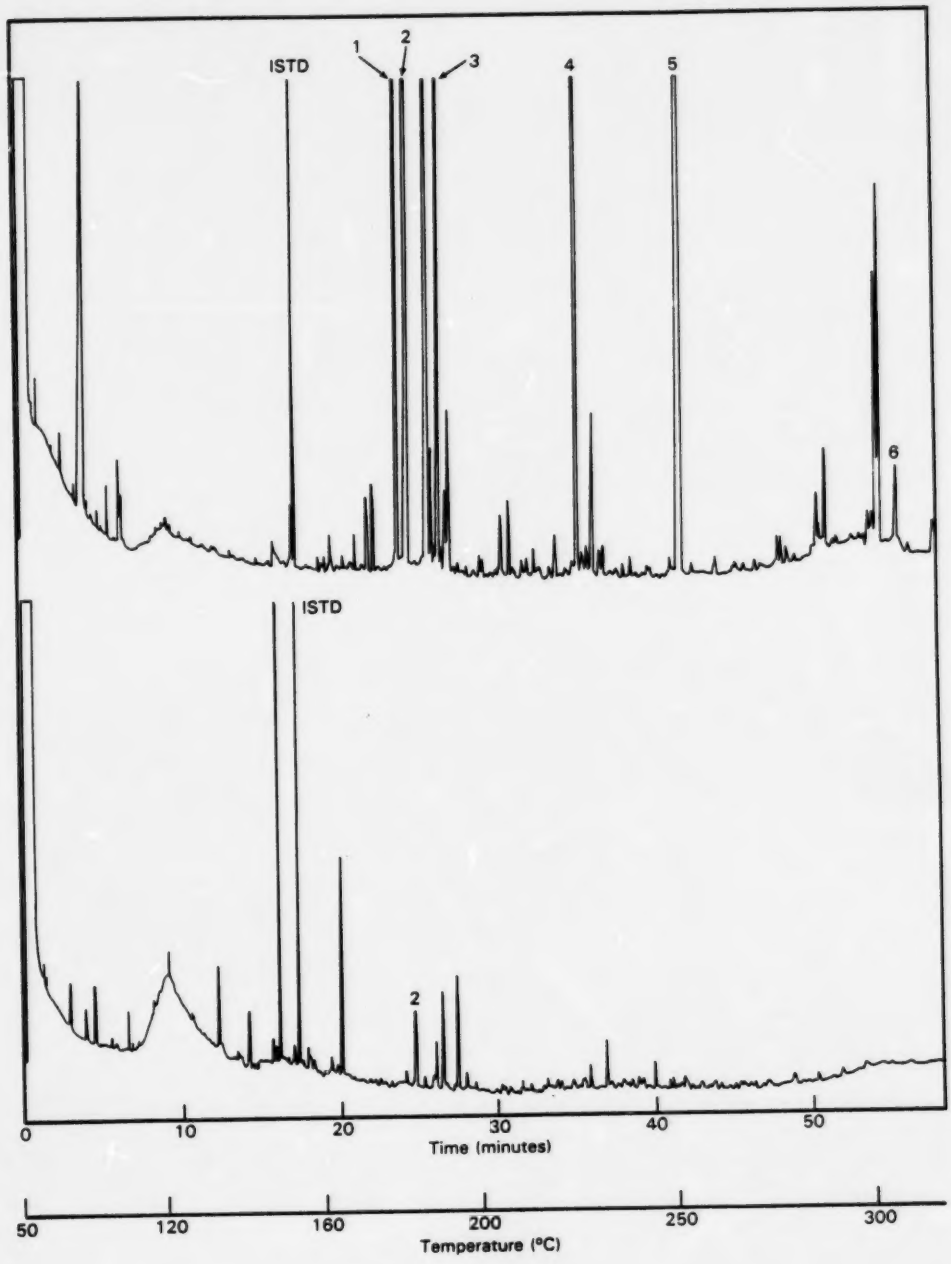

Figure 8. Typical capillary gas chromatograms of adsorbent extracts. Top: Supercritical fluid extract obtained from XAD-2 resin using the carbon dioxide-methanol fluid mixture. Bottom: Soxhlet extract obtained from above adsorbent after supercritical fluid extraction. Peak identifications: 1 = chrysene, 2 = benzanthrone, 3 = 1-nitropyrene, 4 = dibenzo(a,i)carbazole, 5 = coronene, 6 = rubrene.

identified in the figure legend. The 6-aminochrysene and decacyclene were not detected or quantified by capillary GC in any of the extracts due to degradation in the mixture and low volatility, respectively. Even though cleaned XAD-2 resin adsorbent material was used, non-spiked contaminants were extracted by both the supercritical fluid and Soxhlet extraction methods.

Table 2 gives the supercritical fluid extraction results for the spiked XAD-2 resin adsorbents. The highest percent recoveries (using no special means of extract collection) were achieved using CO_2-methanol and pentane supercritical fluids. The CO_2 fluids at 50° and 150°C gave the poorest recovery results. The fluids of higher solvating power (methanol mixtures and pentane) would be expected to provide more efficient extraction. In general, the extraction efficiency for rubrene was the lowest of any for the six spiked compounds quantified, regardless of the supercritical extraction fluid. These XAD-2 resin supercritical fluid extraction results are shown graphically in Figure 9.

The use of a liquid nitrogen collection technique significantly improved the extraction efficiency results for the supercritical CO_2 at 150°C (see Table 2). The low recovery results of the supercritical CO_2 extraction at 150°C were due more to poor collection methods than to poor extraction efficiencies, evidenced by the increased recoveries achieved with liquid nitrogen collection. Using liquid nitrogen collection, the supercritical fluid extraction efficiencies for all the spiked compounds were better for the CO_2 at 150°C than for either the CO_2-methanol or pentane fluid systems. Losses of extracted materials due to aerosol formation or volatility caused lower recoveries without liquid nitrogen collection. Additional details of the liquid nitrogen collection will be discussed later.

The methylene chloride Soxhlet extraction results for the spiked XAD-2 resin adsorbent are given in Table 3. The resin, equilibrated at 10 and 80% humidity, was spiked at 5 and 50 ppm levels with the model compounds. Significantly higher extraction efficiencies were achieved at the 50 ppm spike level compared to the 5 ppm spike level for the 10% humidity XAD-2 resin. All Soxhlet extraction efficiencies were higher than those obtained from the supercritical fluid extractions (see Table 2). As in the supercritical fluid extraction, rubrene showed the lowest recovery results of all the spiked compounds

TABLE 2. XAD RESIN SUPERCRITICAL FLUID EXTRACTION RESULTS

Compound	Extraction Fluid					
	CO_2:MeOH	Pentane	Pentane:EtOH	CO_2(50°C)	CO_2(150°C)	CO_2(150°C) with Liquid Nitrogen Collection
Chrysene						
µg/g spiked	50	49	49	52	49.5	55
µg/g recovered	30	25	15	13	1.1	71
% recovered	60%	51%	31%	25%	2.2%	75%
Benzanthrone						
µg/g spiked	58	57	57	59	57	53
µg/g recovered	36	38	20	17	1.4	42
% recovered	62%	67%	35%	28%	2.5%	79%
1-Nitropyrene						
µg/g spiked	48	47	47	49	47	60
µg/g recovered	14	19	9.5	12	0.86	50
% recovered	29%	40%	20%	24%	1.8%	83%
Dibenzo[a,i]carbazole						
µg/g spiked	49	48	48	50	48	68.5
µg/g recovered	32	25	1.7	5.1	3.0	65
% recovered	65%	52%	3.5%	10%	6.3%	95%
Coronene						
µg/g spiked	45	44	44	46	44	59
µg/g recovered	28	26	16	3.0	3.6	48
% recovered	62%	59%	36%	6.5%	8.2%	81%
Rubrene						
µg/g spiked	48	47	47	49	47	65
µg/g recovered	3.0	7.2	4.7	--	--	16
% recovered	6.2%	15%	10%	0%	0%	25%

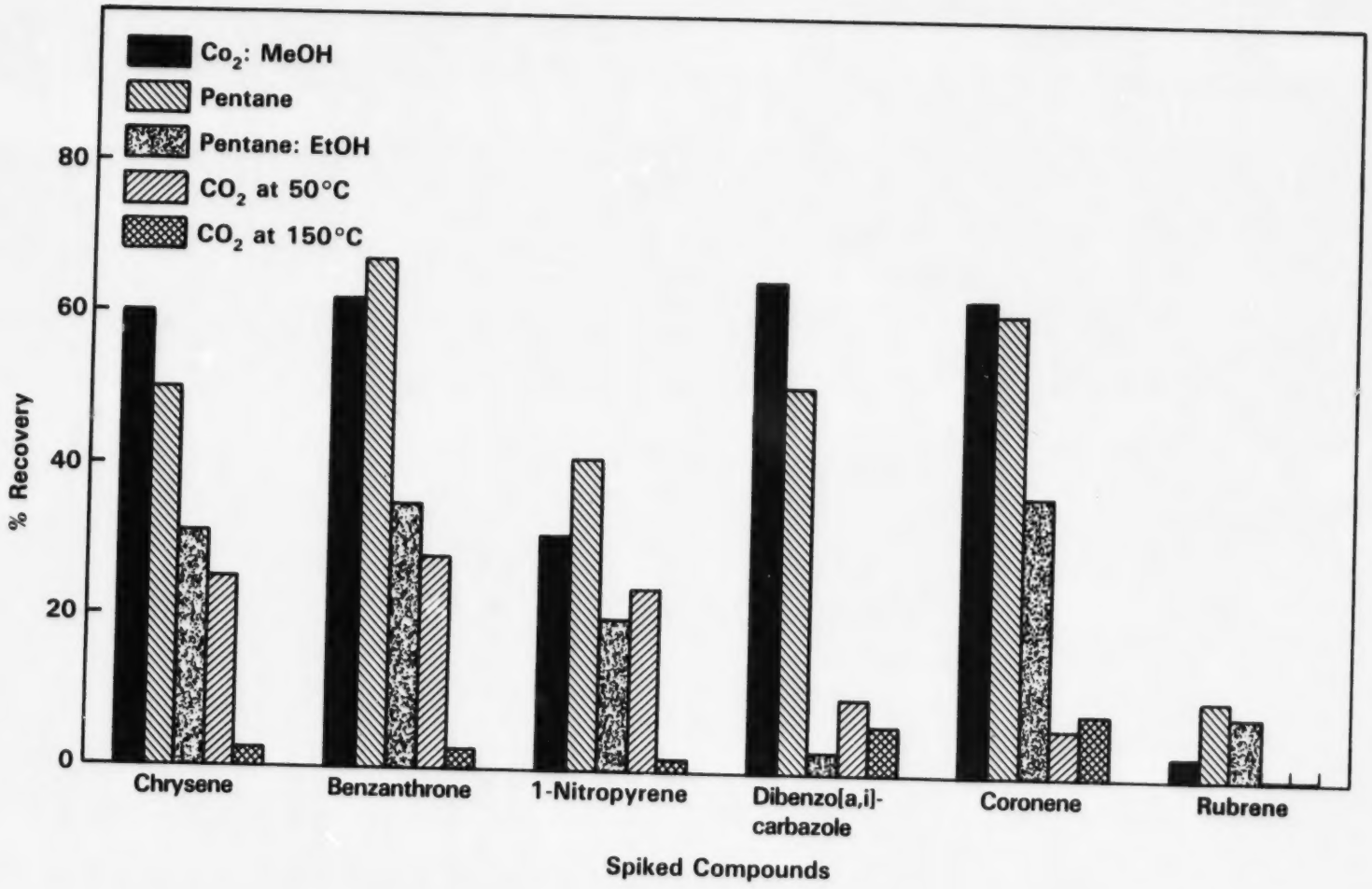

Figure 9. Recovery results for supercritical fluid extractions of XAD resin.

TABLE 3. XAD RESIN METHYLENE CHLORIDE SOXHLET EXTRACTION RESULTS

Compound	Conditions			
	10% Humidity 50 ppm	10% Humidity 5 ppm	80% Humidity 50 ppm	80% Humidity 5 ppm
Chrysene				
µg/g spiked	43	4.7	51	5.2
µg/g recovered	37	2.7	40	4.4
% recovered	86%	57%	78%	85%
Benzanthrone				
µg/g spiked	50	5.4	59	6.0
µg/g recovered	45	3.8	48	5.9
% recovered	90%	70%	81%	98%
1-Nitropyrene				
µg/g spiked	42	4.5	49	5.0
µg/g recovered	42	2.9	44	4.5
% recovered	100%	64%	90%	90%
Dibenzo[a,i]carbazole				
µg/g spiked	42.5	4.6	50	5.1
µg/g recovered	42.5	3.0	44	4.8
% recovered	100%	65%	88%	94%
Coronene				
µg/g spiked	39	4.2	45.5	4.6
µg/g recovered	37.5	3.0	32	4.2
% recovered	96%	71%	70%	91%
Rubrene				
µg/g spiked	41	4.5	49	4.9
µg/g recovered	16	0.35	18	0.88
% recovered	39%	7.8%	37%	18%

using Soxhlet extraction. No additional material was recovered from subsequent methanol Soxhlet extraction of the resin.

After each supercritical fluid extraction, the XAD-2 resins were additionally Soxhlet-extracted with methylene chloride. The quantitative GC results from the analysis of these Soxhlet extracts are given in Table 4 for each of the various supercritical extraction fluids. Little to no additional spiked material was Soxhlet-extracted from the supercritical-fluid-extracted resins, except for the CO_2 supercritical fluid extraction at 50°C. The high additional recovery levels of the spiked compounds with Soxhlet extraction after supercritical CO_2 extraction at 50°C again indicated CO_2 was the poorest supercritical extraction fluid. This is reasonable since at the lower temperatures, adsorption forces would be stronger and extraction would be more difficult. However, at the higher temperature the reduced density (and intrinsic solvent power) is substantially lower (1.3 compared to 2). The low recoveries obtained from the Soxhlet extraction after supercritical extraction with CO_2-methanol, pentane, pentane-ethanol, and CO_2 at 150°C indicated that these supercritical fluids gave nearly comparable extraction results as Soxhlet extraction with methylene chloride. The lower extraction efficiencies of the supercritical fluids (Table 2) versus Soxhlet extraction (Table 3) were probably due to poor collection techniques as mentioned above. The supercritical fluid extractions were more rapid than the Soxhlet extractions, however, requiring only one to two hours for the former versus 16 to 18 hours for the latter.

The Soxhlet-extraction GC quantitative results both before and after supercritical fluid extraction are shown graphically in Figure 10. Again, these data show the low recoveries of Soxhlet-extractable material after the various supercritical fluid extractions, with the exception of the supercritical CO_2 at 50°C.

SK-4 Activated Carbon

Supercritical fluid extraction efficiencies were poor for the model compounds spiked onto the SK-4 activated carbon adsorbent. This adsorbent would have been expected to provide the strongest adsorption interactions and hence the poorest extraction recoveries. Regardless of the extraction fluid, no

TABLE 4. XAD RESIN METHYLENE CHLORIDE SOXHLET EXTRACTION RESULTS AFTER SUPERCRITICAL FLUID EXTRACTION

Compound	Extraction Fluid				
	CO_2:MeOH	Pentane	Pentane:EtOH	CO_2(50°C)	CO_2(150°C)
Chrysene					
µg/g spiked	50	49	49	52	49.5
µg/g recovered	--	--	0.49	4.3	--
% recovered	0%	0%	1.0%	8.2%	0%
Benzanthrone					
µg/g spiked	58	57	57	59	57
µg/g recovered	0.94	7.5	0.74	2.8	0.50
% recovered	1.6%	13%	1.3%	4.7%	0.9%
1-Nitropyrene					
µg/g spiked	48	47	47	49	47
µg/g recovered	--	--	--	1.3	--
% recovered	0%	0%	0%	2.6%	0%
Dibenzo[a,i]carbazole					
µg/g spiked	49	48	48	50	48
µg/g recovered	--	--	0.33	23	0.41
% recovered	0%	0%	0.7%	46%	0.9%
Coronene					
µg/g spiked	45	44	44	46	44
µg/g recovered	--	--	0.23	28	3.3
% recovered	0%	0%	0.5%	61%	7.5%
Rubrene					
µg/g spiked	48	47	47	49	47
µg/g recovered	--	--	--	14	1.8
% recovered	0%	0%	0%	28%	3.8%

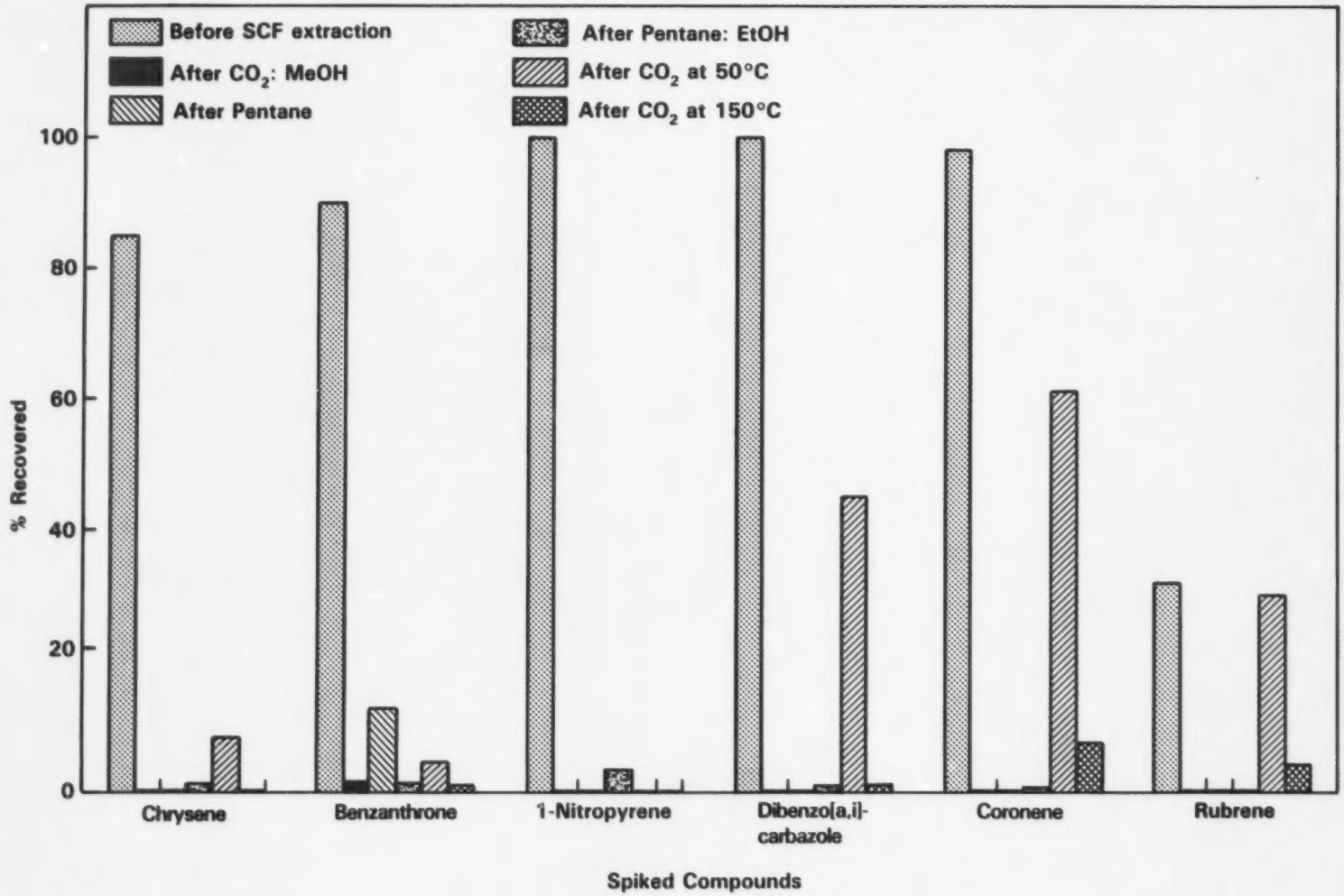

Figure 10. Recovery results for Soxhlet extractions of XAD resin.

more than 4% of any individual compound was recovered in any of the extracts. Supercritical-fluid-extraction GC quantitative recovery results for the activated carbon adsorbent are given in Table 5 and are shown in Figure 11. In most cases, none of the spiked model compounds were recovered from this adsorbent. The pentane-ethanol supercritical fluid gave the best extraction efficiencies of the four supercritical fluid systems evaluated, possibly because of the higher extraction temperature (215°C).

Poor extraction efficiencies were also obtained for the spiked model compounds when the activated carbon adsorbent was Soxhlet-extracted with carbon disulfide (see Table 6). Similar extraction results were obtained for both the 10 and 80% humidity-equilibrated adsorbents. Wide variations between replicate analyses were noted. The Soxhlet extraction appeared to recover slightly higher concentrations of the spiked model compounds compared to the supercritical fluid extractions (see Table 5). In contrast to the extraction results from the XAD-2 resin, rubrene was the component of highest recovery from the activated carbon. This could perhaps be accounted for by a weaker adsorptive interaction with this large molecule.

Table 7 gives the quantitative GC results from the analyses of the carbon disulfide Soxhlet extracts obtained after the supercritical fluid extractions with CO_2-methanol, pentane, pentane-ethanol, and CO_2 at 50° and 150°C. Generally, significantly higher concentrations of the spiked model compounds were recovered from the activated carbon using the Soxhlet extraction method after the supercritical fluid extractions, than were extracted by the supercritical fluid methods themselves. For most of the model compounds, comparable or higher amounts were Soxhlet-extracted after supercritical fluid extraction as were Soxhlet-extracted prior to supercritical fluid extraction (see Figure 12). It is possible that the supercritical fluid extraction process slightly altered the nature of the adsorbent (e.g., disruption of pore structures), allowing more efficient Soxhlet extractions.

Polyurethane Foam Plug (PUF)

High concentrations of interfering, chromatographable contaminants were extracted from the PUF adsorbent by the supercritical fluids. These extracted contaminants are believed to have been part of the PUF matrix. Due to the

TABLE 5. ACTIVATED CARBON SUPERCRITICAL FLUID EXTRACTION RESULTS

Compound	Extraction Fluid				
	CO_2:MeOH	Pentane	Pentane:EtOH	CO_2(50°C)	CO_2(150°C)
Chrysene					
µg/g spiked	51	53	46	52	47
µg/g recovered	--	--	0.19	--	--
% recovered	0%	0%	0.4%	0%	0%
Benzanthrone					
µg/g spiked	59	61	53	59	54
µg/g recovered	--	--	0.54	--	--
% recovered	0%	0%	1.0%	0%	0%
1-Nitropyrene					
µg/g spiked	49	51	44	49	45
µg/g recovered	--	--	0.06	--	--
% recovered	0%	0%	0.1%	0%	0%
Dibenzo[a,i]carbazole					
µg/g spiked	50	52	45	51	46
µg/g recovered	--	--	--	0.61	--
% recovered	0%	0%	0%	1.2%	0%
Coronene					
µg/g spiked	46	47	41	46	42
µg/g recovered	--	0.27	1.3	0.26	0.31
% recovered	0%	0.6%	3.2%	0.6%	0.7%
Rubrene					
µg/g spiked	49	50	44	49	45
µg/g recovered	--	--	--	--	--
% recovered	0%	0%	0%	0%	0%

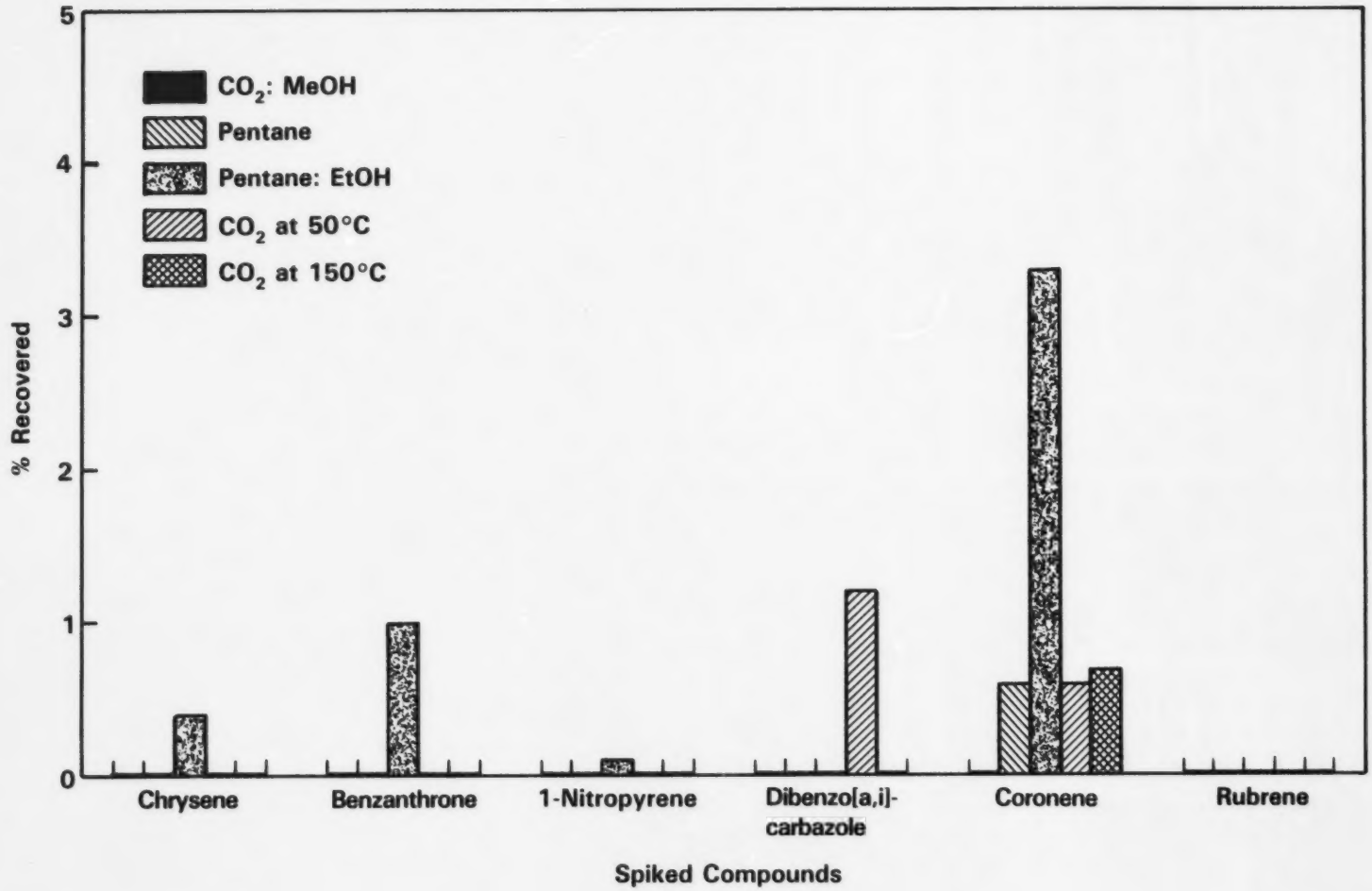

Figure 11. Recovery results for supercritical fluid extractions of activated carbon.

TABLE 6. ACTIVATED CARBON, CARBON DISULFIDE SOXHLET EXTRACTION RESULTS

Compound	Conditions: 10% Humidity 50 ppm Rep 1	10% Humidity 50 ppm Rep 2	80% Humidity 50 ppm Rep 1	80% Humidity 50 ppm Rep 2
Chrysene				
µg/g spiked	45	51	48	54
µg/g recovered	0.61	2.6	0.77	2.3
% recovered	1.4%	5.1%	1.6%	4.3%
Benzanthrone				
µg/g spiked	51	58.5	55	61.5
µg/g recovered	0.39	2.1	1.2	ND(a)
% recovered	0.8%	3.6%	2.2%	
1-Nitropyrene				
µg/g spiked	43	49	46	51
µg/g recovered	0.26	1.2	0.32	1.6
% recovered	0.6%	2.5%	0.7%	3.1%
Dibenzo[a,i]carbazole				
µg/g spiked	44	50	47	52
µg/g recovered	--	--	--	--
% recovered	0%	0%	0%	0%
Coronene				
µg/g spiked	40	45	42	48
µg/g recovered	0.23	0.73	0.38	1.0
% recovered	0.6%	1.6%	0.9%	2.1%
Rubrene				
µg/g spiked	42.5	48	45	51
µg/g recovered	15	12	16	22
% recovered	35%	25%	36%	43%

(a) No data due to interference.

TABLE 7. ACTIVATED CARBON, CARBON DISULFIDE SOXHLET EXTRACTION RESULTS AFTER SUPERCRITICAL FLUID EXTRACTION

Compound	Extraction Fluid				
	CO_2:MeOH	Pentane	Pentane:EtOH	CO_2(50°C)	CO_2(150°C)
Chrysene					
µg/g spiked	51	53	46	52	47
µg/g recovered	2.3	0.72	2.4	0.42	1.4
% recovered	4.5%	1.4%	5.2%	0.8%	3.0%
Benzanthrone					
µg/g spiked	59	61	53	59	54
µg/g recovered	1.8	9.2	4.5	4.1	1.1
% recovered	3.1%	15%	8.5%	7.0%	2.0%
1-Nitropyrene					
µg/g spiked	49	51	44	49	45
µg/g recovered	2.8	3.5	2.5	3.1	0.54
% recovered	5.7%	6.9%	5.7%	6.3%	1.2%
Dibenzo[a,i]carbazole					
µg/g spiked	50	52	45	51	46
µg/g recovered	1.1	0.96	0.11	0.87	--
% recovered	2.2%	1.9%	0.2%	1.7%	0%
Coronene					
µg/g spiked	46	47	41	46	42
µg/g recovered	0.26	--	0.16	0.11	0.19
% recovered	0.6%	0%	0.4%	0.2%	0.5%
Rubrene					
µg/g spiked	49	50	44	49	45
µg/g recovered	0.83	--	1.5	8.5	--
% recovered	1.7%	0%	3.4%	17%	0%

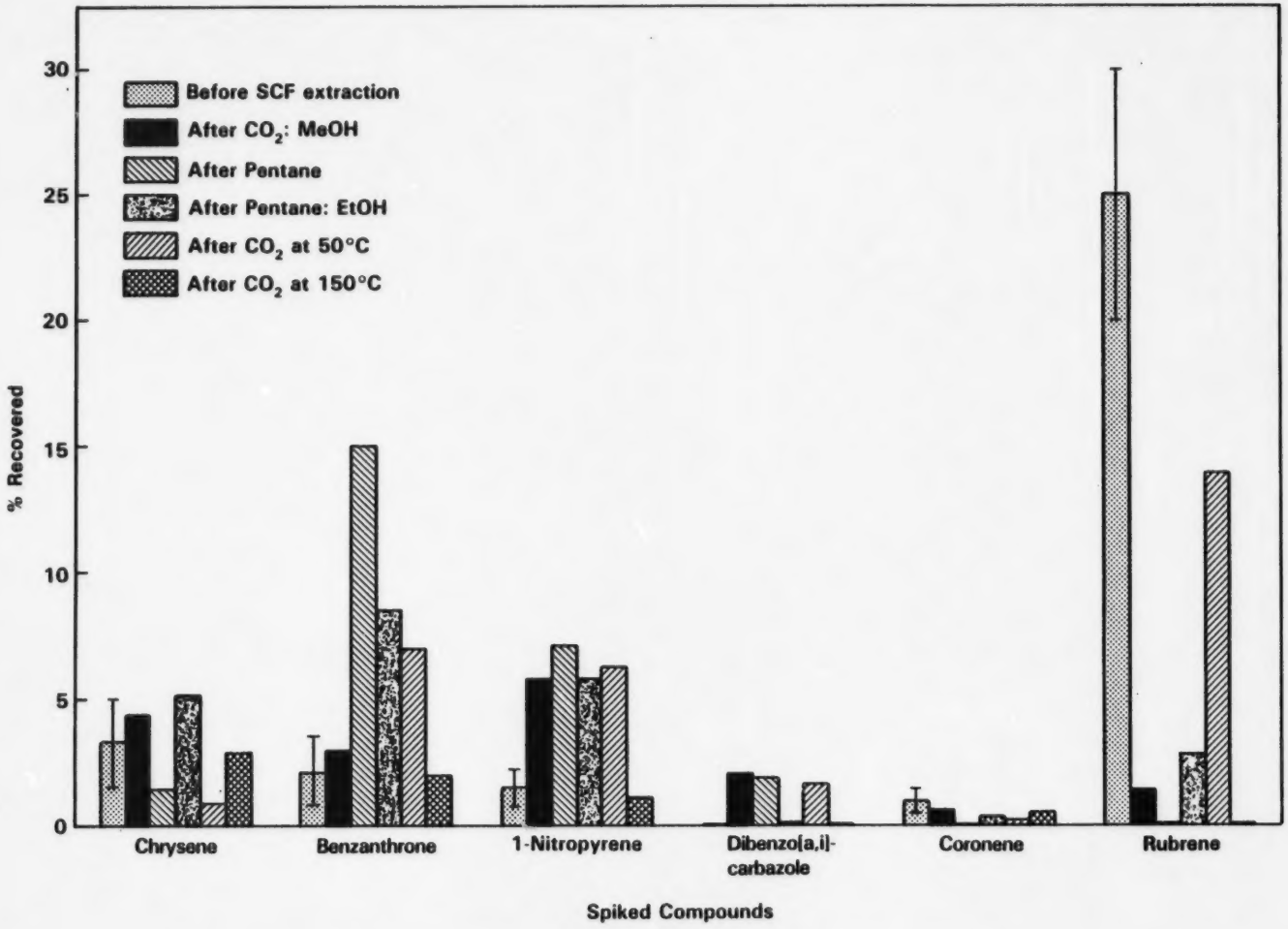

Figure 12. Recovery results of carbon disulfide Soxhlet extractions of activated carbon.

presence of these contaminants, the CO_2-methanol, pentane, and CO_2 at 50°C supercritical fluid extracts were purified using column chromatography prior to capillary GC analysis. The extracts were eluted through a column packed with nine grams of alumina (Fischer, Brockman Activity 1, 1.5% H_2O) using 50 ml of benzene. The nitrogen-containing model compounds were not eluted from the alumina column (due to their polarity) and were, therefore, not quantified. The elution of a significant portion of the extract contaminants occurred when more polar solvents were used to elute the nitrogen-containing model compounds. The GC quantitative results from the supercritical fluid extracts of PUF adsorbents are given in Table 8. The highest extraction efficiencies were obtained with supercritical pentane; the lowest extraction efficiencies were obtained with the supercritical CO_2 at 50°C (as was the case with the XAD-2 resin and activated carbon adsorbents). Supercritical fluid extraction results from the three fluid systems are shown graphically in Figure 13.

Comparable or better extraction efficiencies were obtained from the supercritical fluid extractions with pentane and CO_2-methanol compared to the Soxhlet extractions with methylene chloride. These results are given in Table 9. In addition, little or no additional material was Soxhlet-extracted from the PUF adsorbent after supercritical fluid extraction with CO_2-methanol or pentane (see Table 10). However, significant amounts of the model compounds were additionally Soxhlet-extracted from the PUF that had been previously extracted with supercritical CO_2 at 50°C. These results again showed the inadequacy of the CO_2 fluid at 50°C. The GC quantitative results from the Soxhlet extractions are shown graphically in Figure 14. The shorter extraction times and comparable extraction efficiencies of two of the three supercritical fluid extractions show the potential advantages of supercritical fluid extraction over Soxhlet extraction. The extraction of contaminants from the PUF matrix is a disadvantage of the supercritical fluid extraction method, however. Supercritical fluid extraction to clean the PUF prior to spiking may help eliminate this problem.

NBS Urban Dust

The extraction of the NBS Urban Dust, SRM 1649, was representative of an air particulate extraction. Supercritical fluid extractions were performed using CO_2-methanol, pentane, pentane-ethanol and CO_2 at 50°C to compare results

TABLE 8. PUF SUPERCRITICAL FLUID EXTRACTION RESULTS[a]

Compound	Extraction Fluid		
	CO_2:MeOH	Pentane	CO_2(50°C)
Chrysene			
µg/g spiked	57	48	50
µg/g recovered	45	43	9.6
% recovered	79%	90%	19%
Benzanthrone			
µg/g spiked	65.5	55	57
µg/g recovered	58	49	11.5
% recovered	89%	89%	20%
Coronene			
µg/g spiked	51	43	45
µg/g recovered	46	43	1.9
% recovered	90%	100%	4.25%
Rubrene			
µg/g spiked	54	46	47.5
µg/g recovered	32	64	3.5
% recovered	59%	140%	7.4%

(a) Prior to GC analysis, the extracts were eluted through alumina to remove interfering PUF extracted material. See text for conditions.

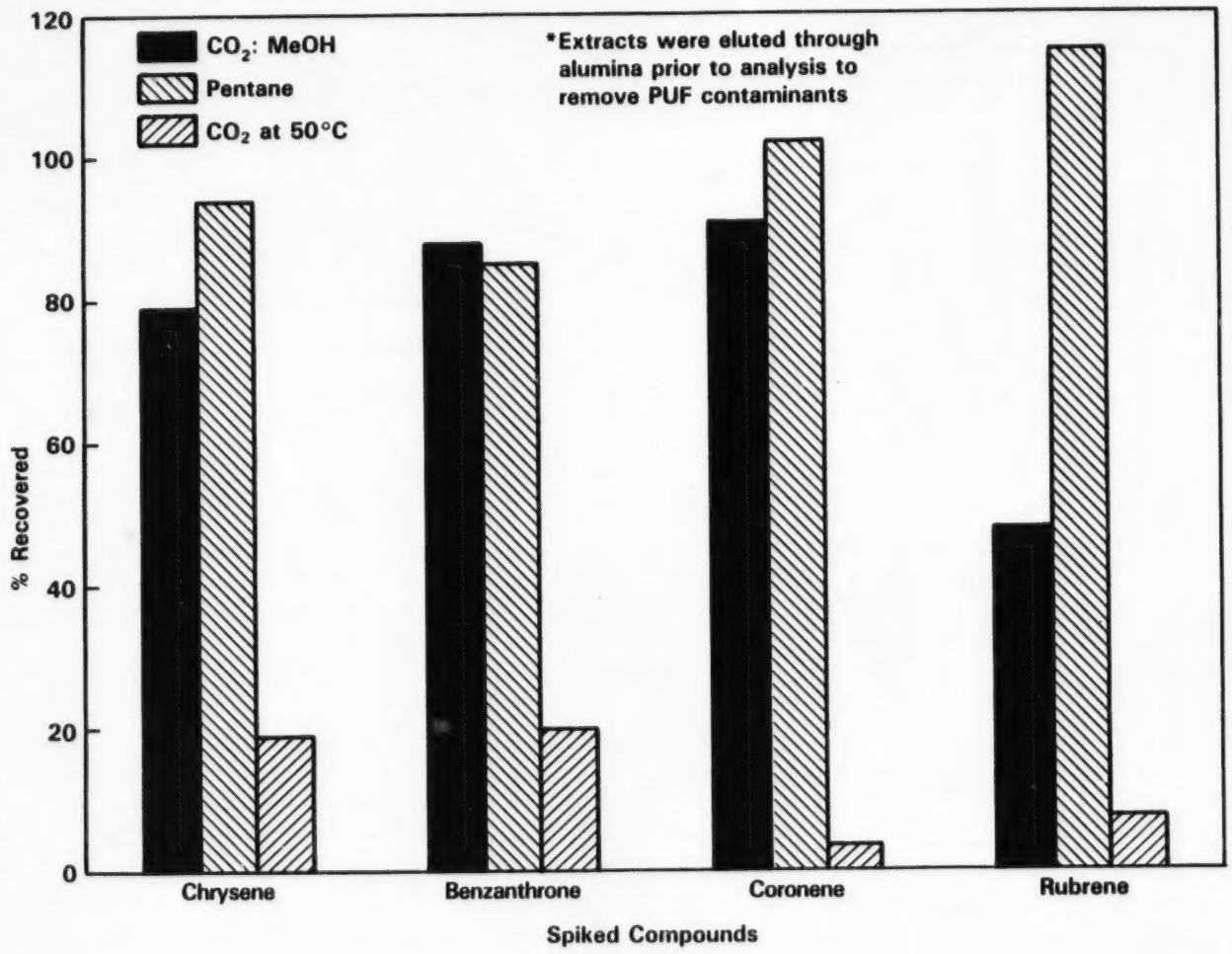

Figure 13. Recovery results for supercritical fluid extractions of PUF.

TABLE 9. PUF METHYLENE CHLORIDE SOXHLET EXTRACTION RESULTS

Compound	Conditions	
	10% Humidity 50 ppm	80% Humidity 50 ppm
Chrysene		
µg/g spiked	65	51
µg/g recovered	50	37
% recovered	77%	73%
Benzanthrone		
µg/g spiked	74.5	59
µg/g recovered	64	48
% recovered	86%	81%
1-Nitropyrene		
µg/g spiked	62	49
µg/g recovered	69	40
% recovered	110%	82%
Dibenzo[a,i]carbazole		
µg/g spiked	64	50
µg/g recovered	60.5	46
% recovered	95%	92%
Coronene		
µg/g spiked	58	46
µg/g recovered	44	36
% recovered	76%	78%
Rubrene		
µg/g spiked	62	49
µg/g recovered	37	32
% recovered	60%	65%

TABLE 10. PUF METHYLENE CHLORIDE SOXHLET EXTRACTION RESULTS AFTER SUPERCRITICAL FLUID EXTRACTION

Compound	Extraction Fluid		
	CO_2:MeOH	Pentane	CO_2(50°C)
Chrysene			
µg/g spiked	57	48	50
µg/g recovered	--	--	2.0
% recovered	0%	0%	4.0%
Benzanthrone			
µg/g spiked	65.5	55	57
µg/g recovered	--	3.7	18
% recovered	0%	6.7%	32%
Coronene			
µg/g spiked	51	43	45
µg/g recovered	--	--	42
% recovered	0%	0%	93%
Rubrene			
µg/g spiked	54	46	47.5
µg/g recovered	--	--	7.0
% recovered	0%	0%	15%

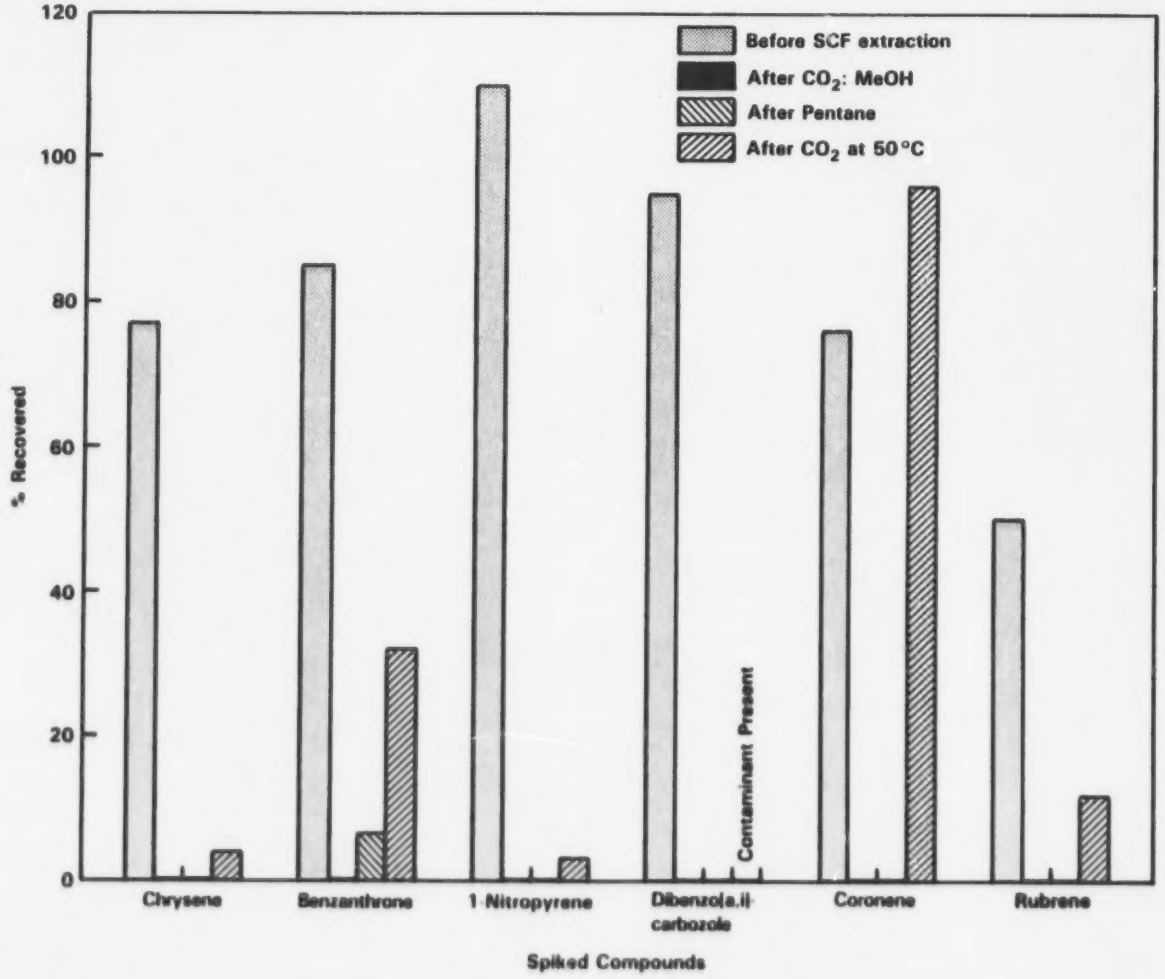

Figure 14. Recovery results for methylene chloride Soxhlet extractions of PUF.

to Soxhlet extraction with methylene chloride. Additional Soxhlet extractions were also performed using the supercritical-fluid-extracted Urban Dust samples. All extracts were analyzed by capillary GC; the components with retention times corresponding to polycyclic aromatic hydrocarbon (PAH) standards as well as other major unidentified components were quantified. A typical chromatogram of an Urban Dust extract is shown in Figure 15. The complexity of the extract is evident from the lack of chromatographic resolution after about 40 minutes of analysis.

The concentration of selected components in the supercritical fluid extracts from the NBS Urban Dust are given in Table 11. The peak numbers given in Table 11 correspond to the peaks labeled in Figure 15. Response factors from closely eluting PAH compounds were used for the quantitative calculations of the unknown components identified only by retention time (RT). These unknown components were the major constituents of the extracts, while the PAH compounds were more minor components in the complex mixtures. The PAH components tentatively identified and quantified in Table 11 may also represent co-eluting species since no mass spectral data was acquired to confirm their presence.

The data for the 25 components given in Table 11 are shown graphically in Figure 16. Some components appeared to be selectively extracted by the different supercritical fluids. For example, component 6 appeared in high concentration in the CO_2-methanol and CO_2 at 50°C supercritical fluid extracts, but little to none was detected in the pentane and pentane-ethanol extracts. Other wide variations between component concentrations in the supercritical extracts occurred with components 4, 5, 10, 14 and 16. The pentane-ethanol and CO_2-methanol fluids gave the best overall supercritical extraction results based on the concentrations of these 25 components. The supercritical pentane appeared to generally extract less material than the other three fluids (although more material may have been lost during collection with the pentane).

Soxhlet extraction results were quite similar to the pentane-ethanol and CO_2-methanol supercritical fluid extraction quantitative results. The methylene chloride Soxhlet-extraction GC quantitative results are given in Table 12 and are shown graphically in Figure 17. Significantly higher amounts of some components (most notably components 4 and 6) were extracted by the supercritical fluids compared to Soxhlet extraction.

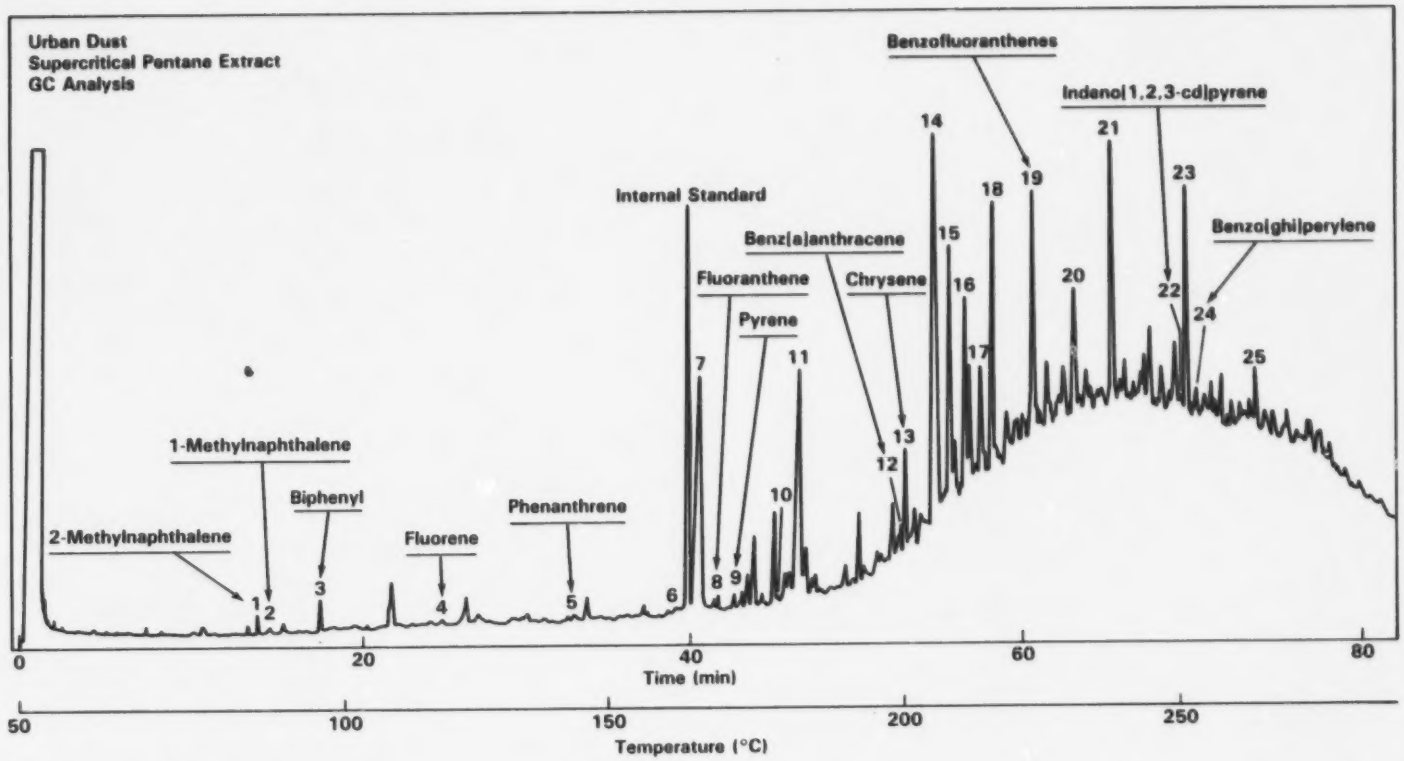

Figure 15. Capillary GC chromatogram of Urban Dust supercritical pentane extract. Peak numbers identify components described in Figures 16-18.

TABLE 11. CONCENTRATION (μg/g) OF SELECTED COMPONENTS IN NBS URBAN DUST (1649) EXTRACTED BY SUPERCRITICAL FLUIDS

Peak No.[a]	Compound[b]	Extraction Fluid			
		CO_2:MeOH	Pentane	Pentane:EtOH	CO_2(50°C)
1	2-Methylnaphthalene	1.2	1.1	3.6	--
2	1-Methylnaphthalene	4.7	0.74	--	--
3	Biphenyl	4.8	1.8	6.6	1.1
4	Fluorene	7.0	--[c]	--	42
5	Phenanthrene	3.0	0.52	3.4	72
6	RT 38.92	66	0.03	--	21
7	RT 40.50	110	51	148	170
8	Fluoranthene	3.4	1.1	4.8	17
9	Pyrene	2.9	1.2	7.1	18
10	RT 45.17	34	0.62	2.9	650
11	RT 46.45	100	47	142	380
12	Benz[a]anthracene	0.80	3.5	--	--
13	Chrysene	32	15	30	45
14	RT 54.73	880	100	990	7.2
15	RT 55.49	24	36	88	15
16	RT 56.41	210	32	160	1000
17	RT 57.40	20	15	77	8.6
18	RT 58.05	110	41	88	11
19	Benzofluoranthenes	150	51	140	69
20	RT 62.88	61	24	49	1.7
21	RT 65.20	150	49	130	34
22	Indeno[1,2,3-cd]pyrene	0.60	--	--	--
23	RT 69.60	140	45	110	7.6
24	Benzo[ghi]perylene	9.0	--	--	5.8
25	RT 73.76	14	15	21	5.6

(a) Refers to peaks labelled in Figure 15.
(b) Identifications based on retention time (RT) only, any co-eluting species may also be present.
(c) None detected.

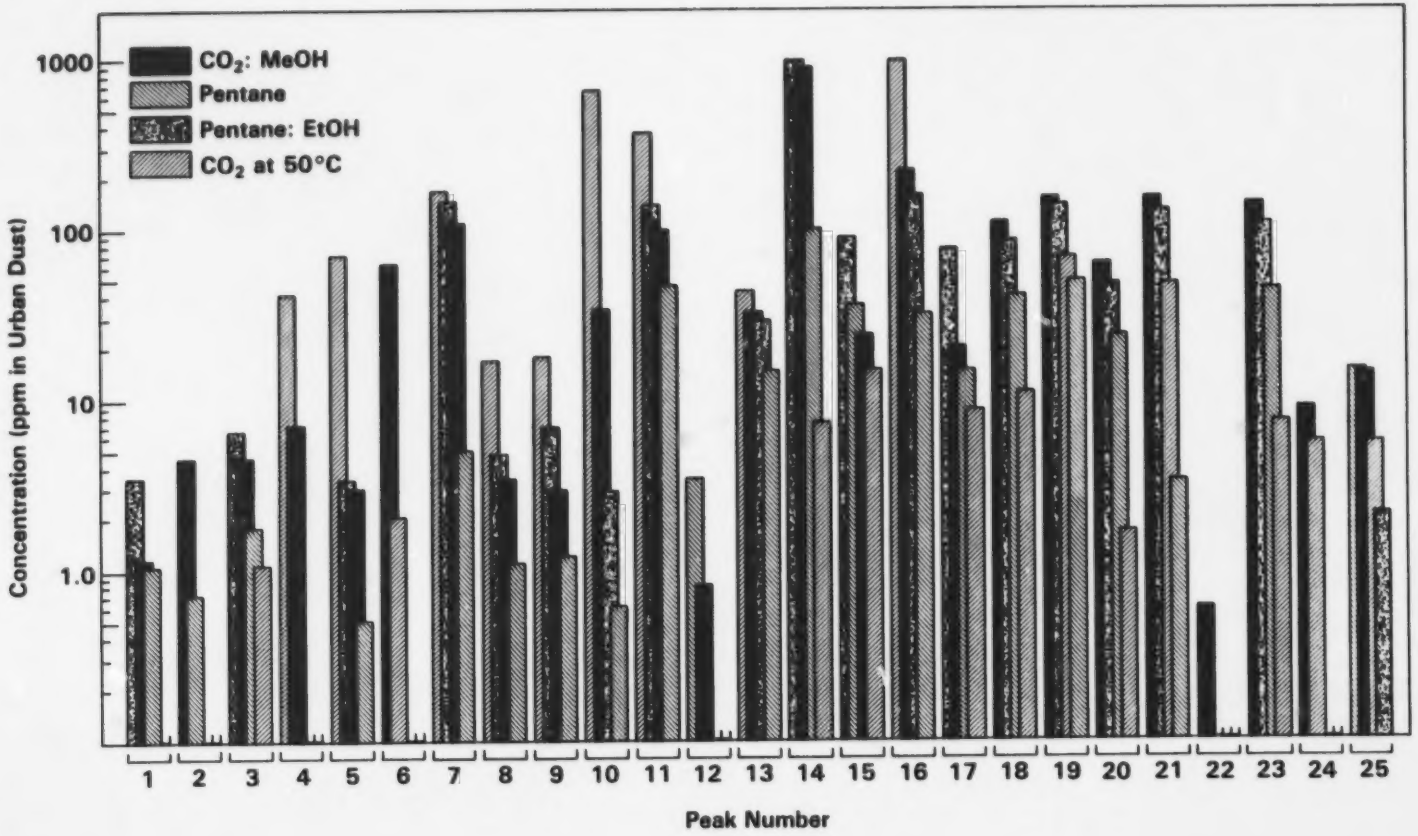
CO_2: MeOH
Pentane
Pentane: EtOH
CO_2 at 50°C
Concentration (ppm in Urban Dust)
1000
100
10
1.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
Peak Number

Figure 16. Concentrations of selected components in supercritical fluid extracts of NBS Urban Dust. Peak numbers refer to components marked in the chromatogram shown in Figure 15.

TABLE 12. CONCENTRATION (μg/g) OF SELECTED COMPONENTS IN NBS URBA DUST (1649) EXTRACTED BY METHYLENE CHLORIDE SOXHLET EXTRACTION BEFORE AND AFTER SUPERCRITICAL FLUID EXTRACTION

Peak No.[a]	Compound[b]	Conditions				
		Soxhlet	After CO_2:MeOH	After Pentane	After Pentane:EtOH	After CO_2(50°C)
1	2-Methylnaphthalene	4.1	--	--	--	1.8
2	1-Methylnaphthalene	0.17	--	--	--	1.6
3	Biphenyl	3.5	0.09	0.04	0.01	3.5
4	Fluorene	--[c]	0.92	--	--	--
5	Phenanthrene	2.2	0.19	0.01	0.01	0.73
6	RT 38.92	--	16	0.15	0.32	--
7	RT 40.50	140	11	8.0	2.8	48
8	Fluoranthene	4.9	0.33	--	--	3.0
9	Pyrene	5.6	1.3	0.55	0.33	2.3
10	RT 45.17	1.1	9.7	0.07	0.22	0.16
11	RT 46.45	150	8.0	4.6	1.8	48
12	Benz[a]anthracene	0.57	--	--	0.03	1.6
13	Chrysene	56	4.6	1.0	2.3	12
14	RT 54.73	1300	76	13	0.12	1400
15	RT 55.49	160	4.6	0.64	2.1	32
16	RT 56.41	200	16	0.40	5.8	150
17	RT 57.40	56	1.2	1.7	0.09	32
18	RT 58.05	90	5.5	0.44	1.6	17
19	Benzofluoranthenes	130	8.4	2.9	1.8	47
20	RT 62.88	48	3.3	0.55	1.3	13
21	RT 65.20	130	7.6	1.0	1.6	54
22	Indeno[1,2,3-cd]-pyrene	1.7	--	--	--	--
23	RT 69.60	120	8.0	6.7	1.5	59
24	Benzo[ghi]perylene	16	1.8	0.03	--	--
25	RT 73.76	24	--	3.1	0.63	26

(a) Refers to peaks in Figures 17 and 18.
(b) Identifications based on retention time (RT) only, any co-eluting species may also be present.
(c) None detected.

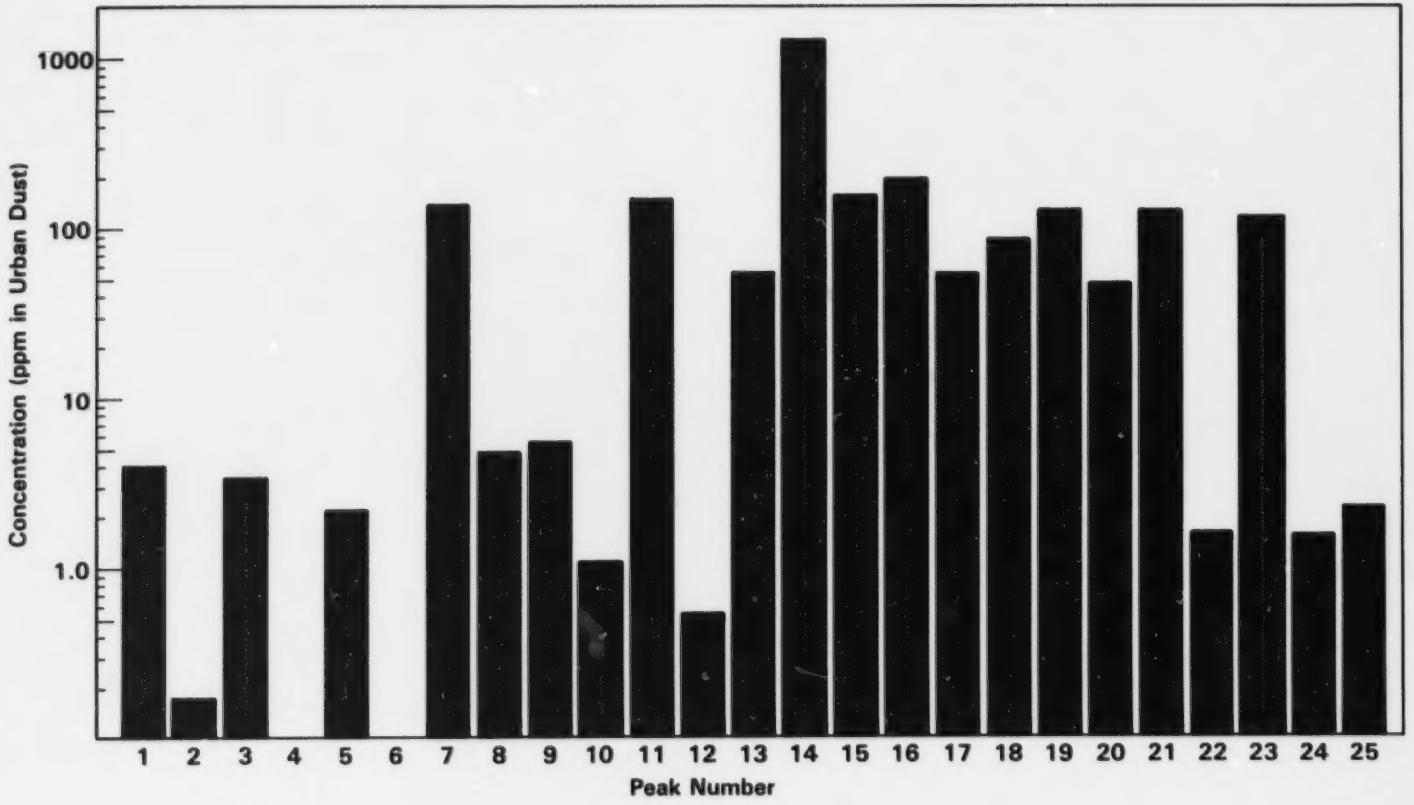

Figure 17. Concentrations of selected components in methylene chloride Soxhlet extracts of NBS Urban Dust. Peak numbers refer to components marked in the chromatogram shown Figure 15.

Soxhlet extraction with methylene chloride after supercritical fluid extractions removed additional organic material from the Urban Dust. The GC quantitative results from these Soxhlet extractions are also given in Table 12. The data is graphically presented in Figure 18. The largest quantity of additional material was extracted from the Urban Dust that had been previously extracted with supercritical CO_2 at 50°C, followed by extraction with supercritical CO_2-methanol. The smallest quantity of organic material (based on these 25 components) was additionally Soxhlet-extracted from the Urban Dust that had been extracted with supercritical pentane and pentane-ethanol fluids. This data, plus the data of Table 11, indicated that a collection problem occurred with the supercritical pentane extract of the Urban Dust, since lower amounts were quantified in this extract, yet little additional material was Soxhlet-extracted. This data, plus the data of Table 11, also indicated that the pentane-ethanol supercritical fluid gave the overall best supercritical extraction results using the techniques employed. More extensive supercritical fluid extraction utilizing larger volumes of extracting fluid would have undoubtedly provided more efficient overall extraction, leaving less material to be Soxhlet-extracted.

Liquid Nitrogen Collection

As has been previously mentioned, some of the low recoveries of components from the spiked adsorbents may have been caused by poor collection techniques during the supercritical fluid extractions. Better collection methods could improve the results achieved by the supercritical fluid extractions since little additional material was Soxhlet-extracted from the XAD-2 resin or Urban Dust after the supercritical fluid extraction with CO_2 at 150°C or pentane, respectively, even though poor extraction efficiencies were obtained. Extracted components appeared to be lost due to volatilization during sample preparation for GC analysis and/or due to aerosol formation during the depressurization of the supercritical fluid into the collection flask. In an attempt to correct this problem, the sample collection flask was sealed and immersed in liquid nitrogen during a supercritical fluid extraction of a spiked XAD-2 resin with CO_2 at 150°C. The entire CO_2 extract was frozen into the collection flask and then allowed to thaw and evaporate when the extraction was completed. The extract obtained in this fashion was then analyzed by capil-

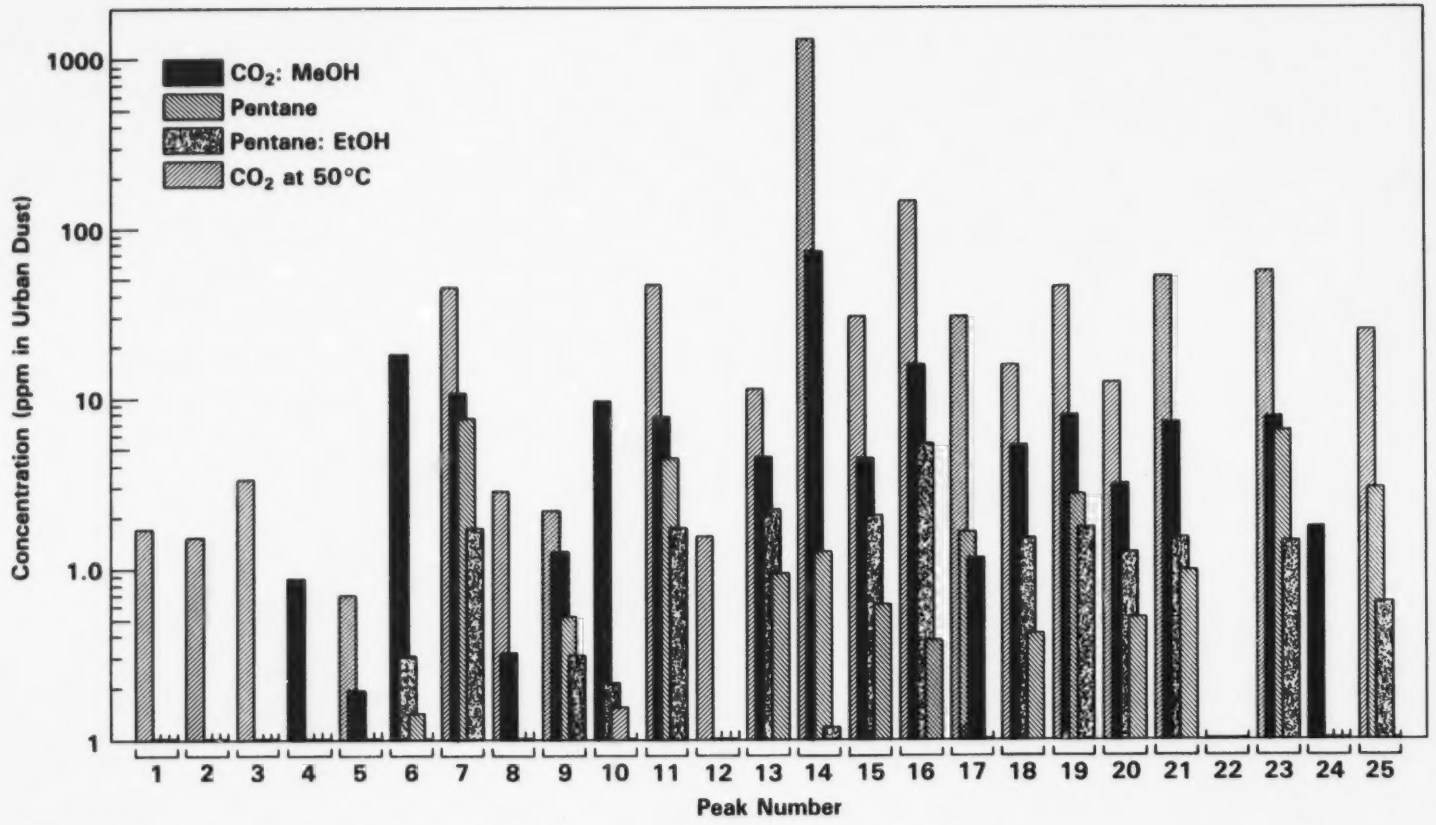

Figure 18. Concentrations of selected components in Soxhlet extracts obtained after supercritical fluid extraction of NBS Urban Dust. Peak numbers refer to components marked in the chromatogram shown in Figure 15.

lary GC to determine the effect of the liquid nitrogen collection; the quantitative GC results have been previously given in Table 2 and are shown in Figure 19. The spiked components that gave poor recoveries with supercritical extraction with CO_2 at 150°C without liquid nitrogen collection gave good recoveries using the same conditions with liquid nitrogen collection. The subsequent Soxhlet extraction recovered only additional high molecular weight coronene and rubrene from the XAD-2 resin, showing overall good extraction results. The potential of supercritical fluid extractions appears much better with the development of improved collection techniques.

DIRECT SUPERCRITICAL FLUID EXTRACTION-MASS SPECTROMETRY

To better understand the extraction process (e.g., solubilization, adsorption interactions, etc.) and have the capability to optimize selective fractionations, it is necessary to understand the extraction kinetics of the components of interest from the specified matrix. Direct supercritical fluid extraction-mass spectrometry provides a means of simultaneously monitoring the extraction behavior of a number of compounds from an adsorbent matrix under a specified set of conditions.

Initial data obtained by this technique for the model compounds extracted from XAD-2 resin with carbon dioxide at 150°C is shown in Figure 20. The slight discontinuity at approximately 100 minutes was probably due to a flow change resulting from partial blockage of the restrictor. The extraction profiles (relative intensity of the major ion from each component versus time) show increased solubility for each compound as the pressure (and solvent power) was increased, and then a decline in intensity as the material was exhausted. The slopes of the rising extraction curves were different for the individual compounds as the pressure was rapidly increased from 73 to 400 atmospheres (first 16 minutes of the extraction), indicating different solubility and/or desorption behavior for each of the components. For instance, the slope of the chrysene curve was more gradual as pressure was increased compared to the decacyclene, which increased very rapidly once a certain pressure was reached. This behavior could be more rigorously evaluated using a slower pressure ramp.

The extraction profiles shown in Figure 20 were each normalized to 100% relative intensity, making absolute comparisons difficult. The normalization

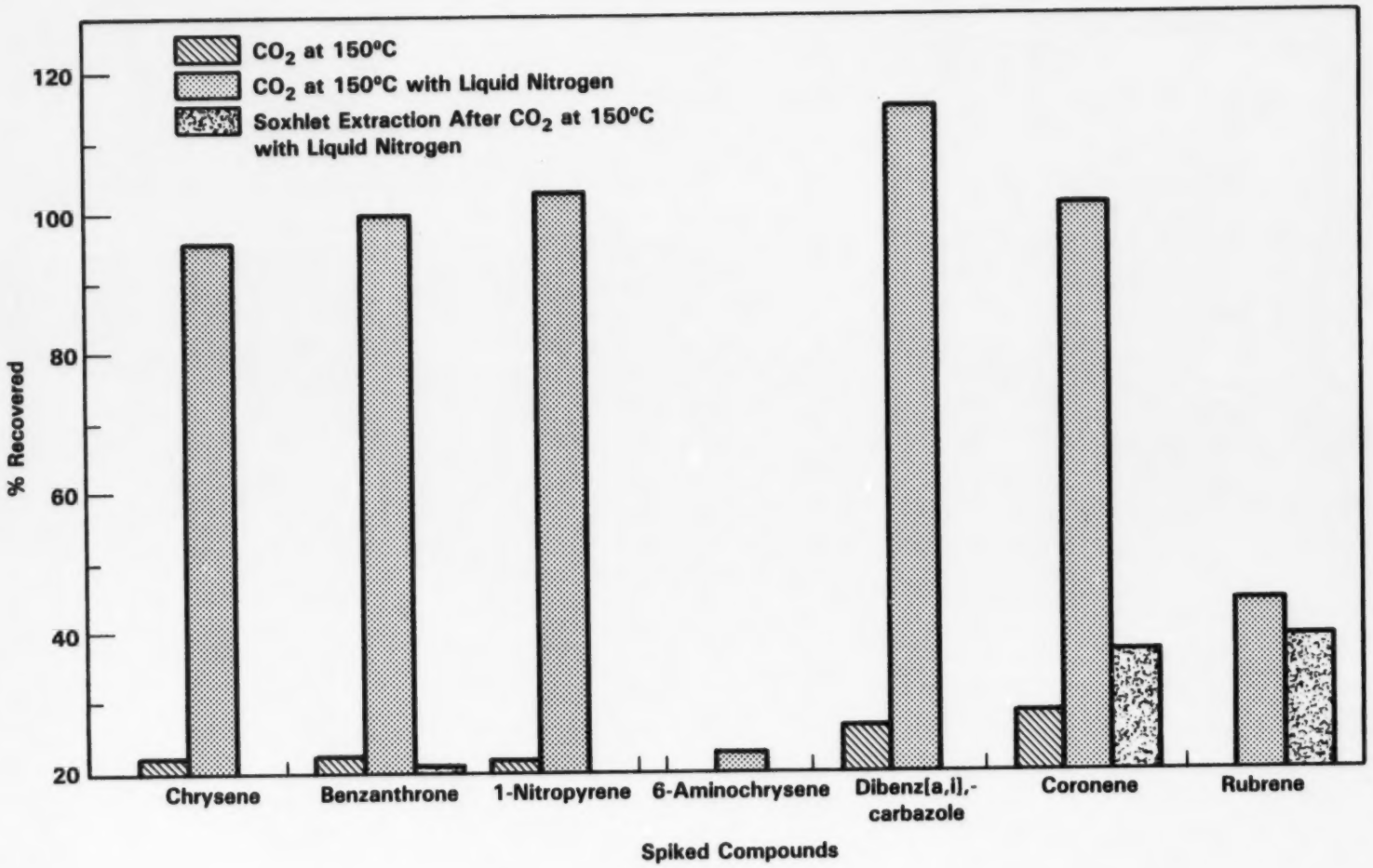

Figure 19. Effect of liquid nitrogen collection of carbon dioxide supercritical fluid extract of XAD resin.

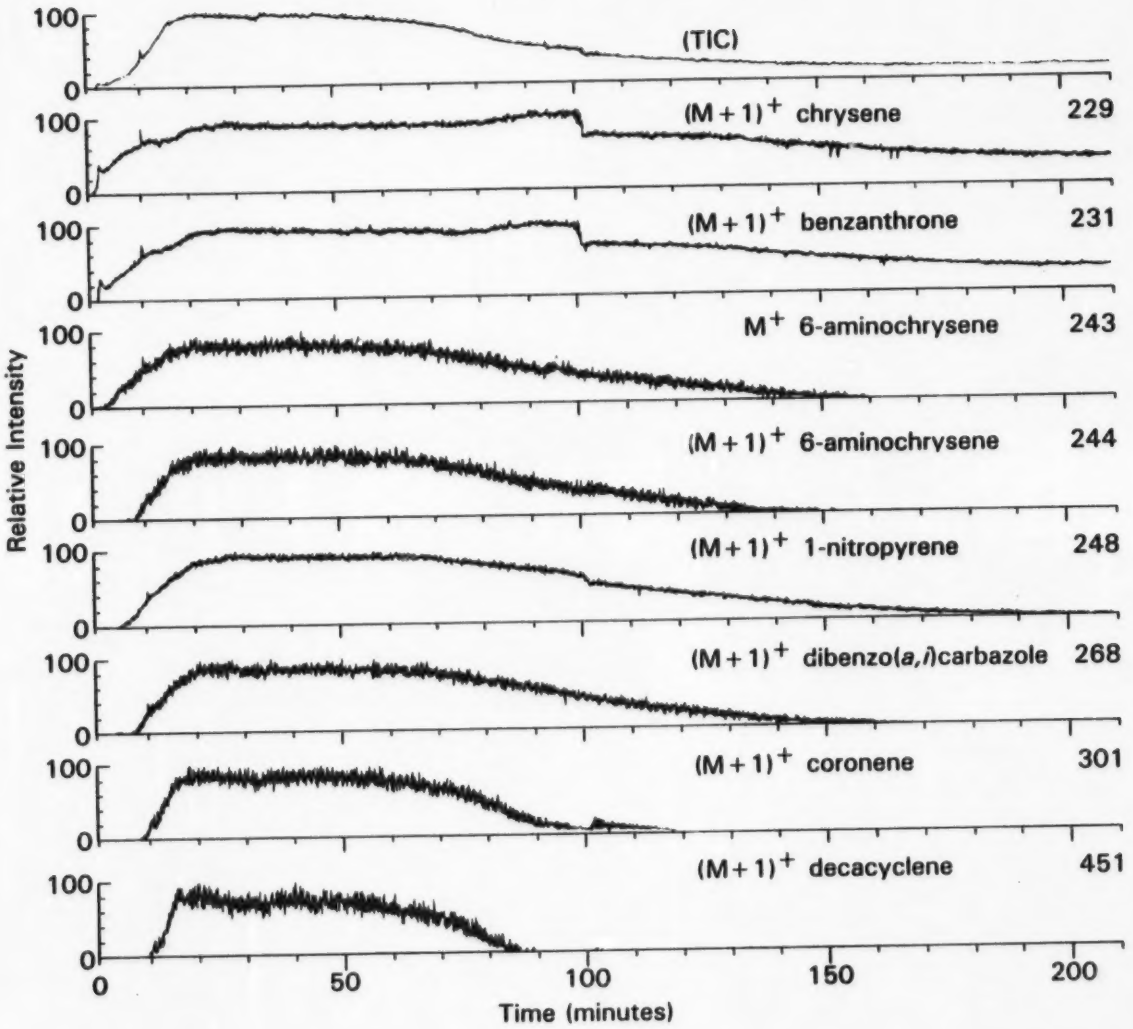

Figure 20. Extraction profiles of the model compounds obtained by SFE-MS with supercritical carbon dioxide from XAD resin.

factors for each component are listed in Table 13. These multipliers ranged between 6 and 38, with the larger values generally corresponding to the heavier molecules. Although the differences in magnitude may be partially accounted for by instrument response (i.e., quadrupole discrimination), they are also indicative of differences in absolute solubility. The more polar components (6-aminochrysene and dibenzo(a,i)carbazole) and the heavier molecular weight components (coronene and decacyclene) would be expected to have lower solubility in supercritical carbon dioxide than the less polar and lower molecular weight materials. This is consistent with the observed normalization factors. An interesting comparison can also be made between benzanthrone and 6-aminochrysene, since they have similar molecular weights and would be expected to have similar instrument response. However, the normalization factor is five times greater for the 6-aminochrysene suggesting lower solubility of approximately the same amount. The consistency in the extraction profiles and the normalization factors for the two ions $(M)^+$ and $(M+1)^+$ of 6-aminochrysene is noteworthy.

Table 13. NORMALIZATION FACTORS FOR EXTRACTION PROFILES

Compound	M/Z	Multiplier
TIC	---	0.8
chrysene	229	8
benzanthrone	231	6
6-aminochrysene	243	30
6-aminochrysene	244	31
1-nitropyrene	248	9
dibenzo(a,i)carbazole	268	25
coronene	301	29
decacyclene	451	38

The differences in the normalization factors make comparisons somewhat difficult, but the exhaustion behavior or decay curves for each of the materials also show compound specific behavior. In general, the lower molecular

weight materials persisted longer and the heavier molecular weight materials exhausted earlier. For instance, the extraction flux of 1-nitropyrene dropped by a factor of two after 100 minutes of extraction, but 200 minutes were required for the same decrease of chrysene. More dramatic behavior was observed for the decacyclene which dropped below detectability limits after only 90 minutes of extraction. This appears somewhat anomalous, since it would be expected that a longer extraction time would be required for a component of lower solubility. Clearly, the extraction process is not completely understood, and additional studies need to be conducted for further insight.

ON-LINE SUPERCRITICAL FLUID EXTRACTION-GAS CHROMATOGRAPHY

A logical extension of supercritical fluid extraction is to combine the extraction process with a chromatographic analysis method. This process provides the basis for simple automated analytical methods without the necessity for prior sample preparation, by instrumentally linking the sample preparation and analysis steps. The variable solvating power of a supercritical fluid provides the mechanism for the selective extraction of the components of interest from the sample matrix. The extraction effluent can then be concentrated on the head of a capillary gas chromatography column in preparation for a typical high-resolution chromatographic separation. This methodology is particularly useful for trace analysis where limited amounts of analyte are present.

Chromatograms illustrating the operation of the on-line supercritical fluid extraction-gas chromatography instrumentation and the selective extraction capability of this method are shown in Figure 21. In this example a simple mixture of PAH components was extracted with supercritical carbon dioxide, concentrated on the head of a capillary column, and then analyzed by capillary gas chromatography. The components in the mixture were selectively extracted by adjusting the solvating power of the carbon dioxide by regulating the pressure. The sample was extracted at progressively higher pressures with three-minute extractions at each pressure being valved into the capillary column for collection and subsequent analysis. At low solvent power, essentially nothing was extracted, as can be observed from the chromatogram of the 75 atmosphere extraction. As the pressure was increased to 150, 200, and

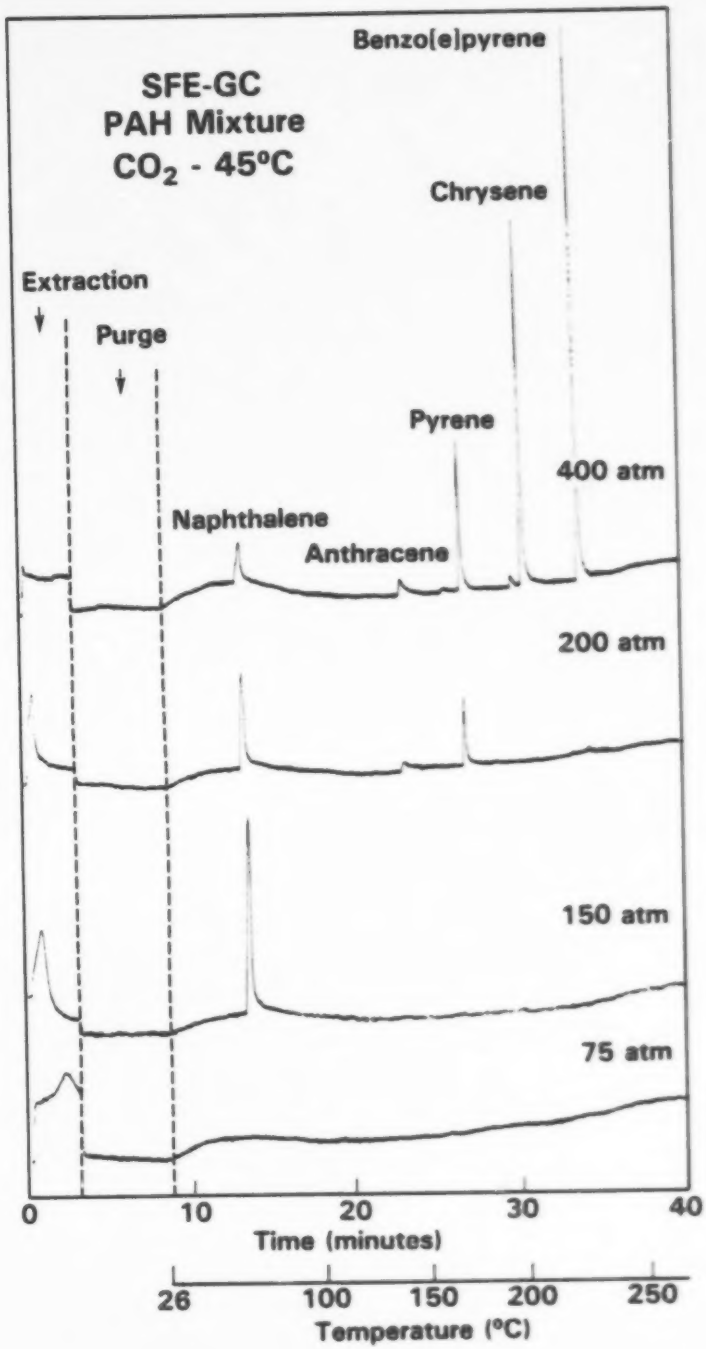

Figure 21. Supercritical fluid extraction-gas chromatography of a PAH mixture. Conditions: 3 min. extractions with carbon dioxide at 45°C, 5 min. purge, temperature programmed from 26 to 250°C at 8°C/min., 15m x 0.25 mm fused silica column coated with SE-54.

finally 400 atmospheres, materials of increasingly larger molecular weight were extracted. At the upper pressure when all the components were extracted, naphthalene was lower in intensity than at earlier pressures, indicating that it was being exhausted from the sample. After each three-minute extraction onto the head of the capillary column, high pressure carrier gas was purged through the restrictor to flush out any remaining materials. The restrictor region was maintained at elevated temperatures (e.g. 250°C) to aid analyte transport through the interface by thermal migration. After the extract was collected on the head of the capillary column, a typical gas chromatographic analysis utilizing temperature programming was conducted. During the chromatographic analysis the extraction effluent was valved to an external collection vessel. However, if an exhaustive extraction had not been desired, the extraction could have been interrupted prior to progressing to the next pressure step.

A different application of this methodology is illustrated in Figure 22 in which NBS Urban Dust (air particles) was analyzed. In these analyses the air particles were extracted with carbon dioxide at three pressures. At the lower pressure a longer extraction time was utilized to deposit more material on the column. Even with a ten-minute versus three-minute extraction time, more material was extracted at 250 atmospheres than at 150 atmospheres. At 250 atmospheres a higher percentage of heavier molecular weight material was extracted, as evidenced by the higher relative peak heights of the later-eluting components. However, much more material with a higher relative percentage of heavier molecular weight compounds was extracted at 350 atmospheres. The rising baselines of the chromatograms indicate a large number of unresolved components, present in low concentration. A more optimized gas chromatographic analysis would have undoubtedly provided better separation of the mixture components. Again, the selective fractionation capability of supercritical fluid extraction is illustrated from these chromatograms.

Another example using slightly different conditions for the extraction-analysis of Urban Dust is shown in Figure 23. Carbon dioxide at 50°C and at two different pressures was used to obtain the selective analyses. At the lower pressure more low molecular weight material was extracted, and at the higher pressure significantly more high molecular weight material was extrac-

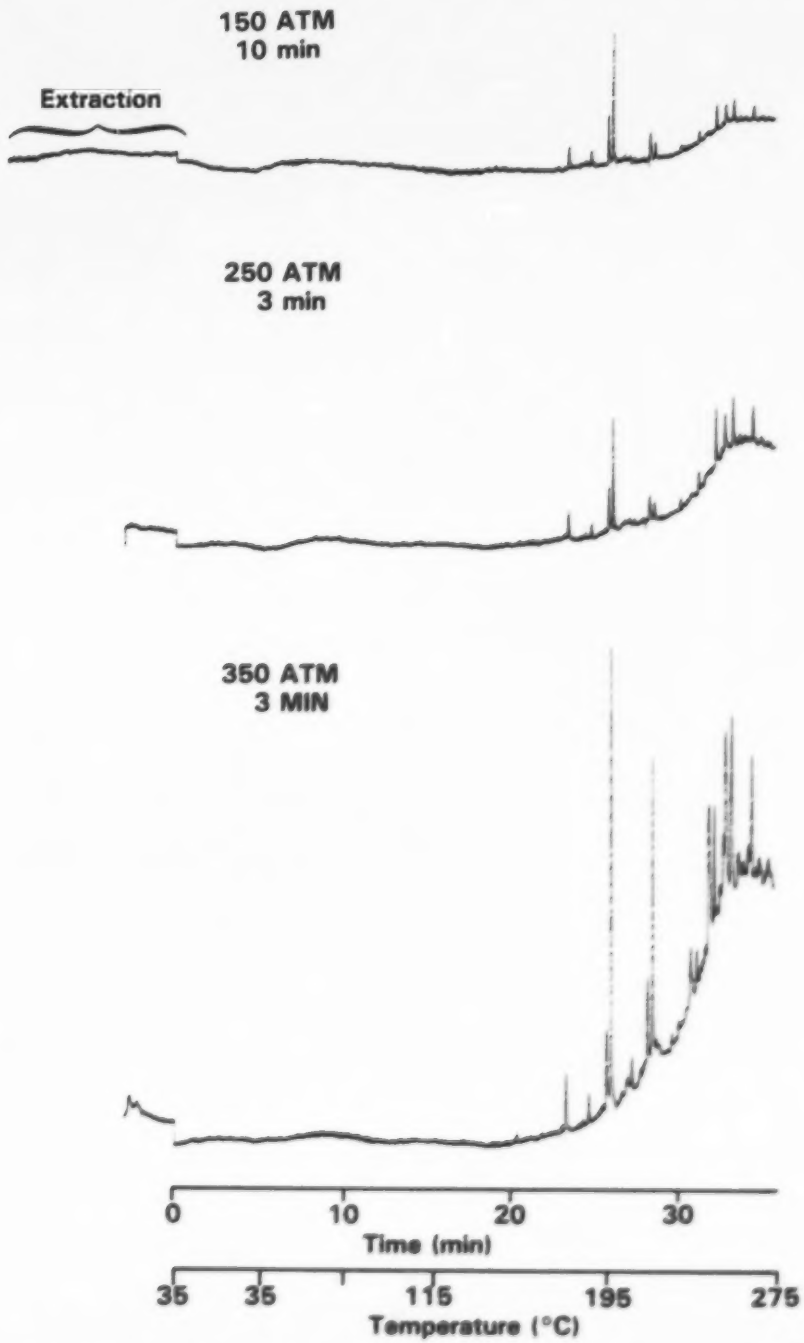

Figure 22. Supercritical fluid extraction-gas chromatography of NBS Urban Dust at three pressures. Conditions: 3-10 min. extractions with carbon dioxide at 40°C, 5 min. purge, temperature programmed from 35 to 275°C at 8°C/min., 15m x 0.25 mm fused silica column coated with SE-54.

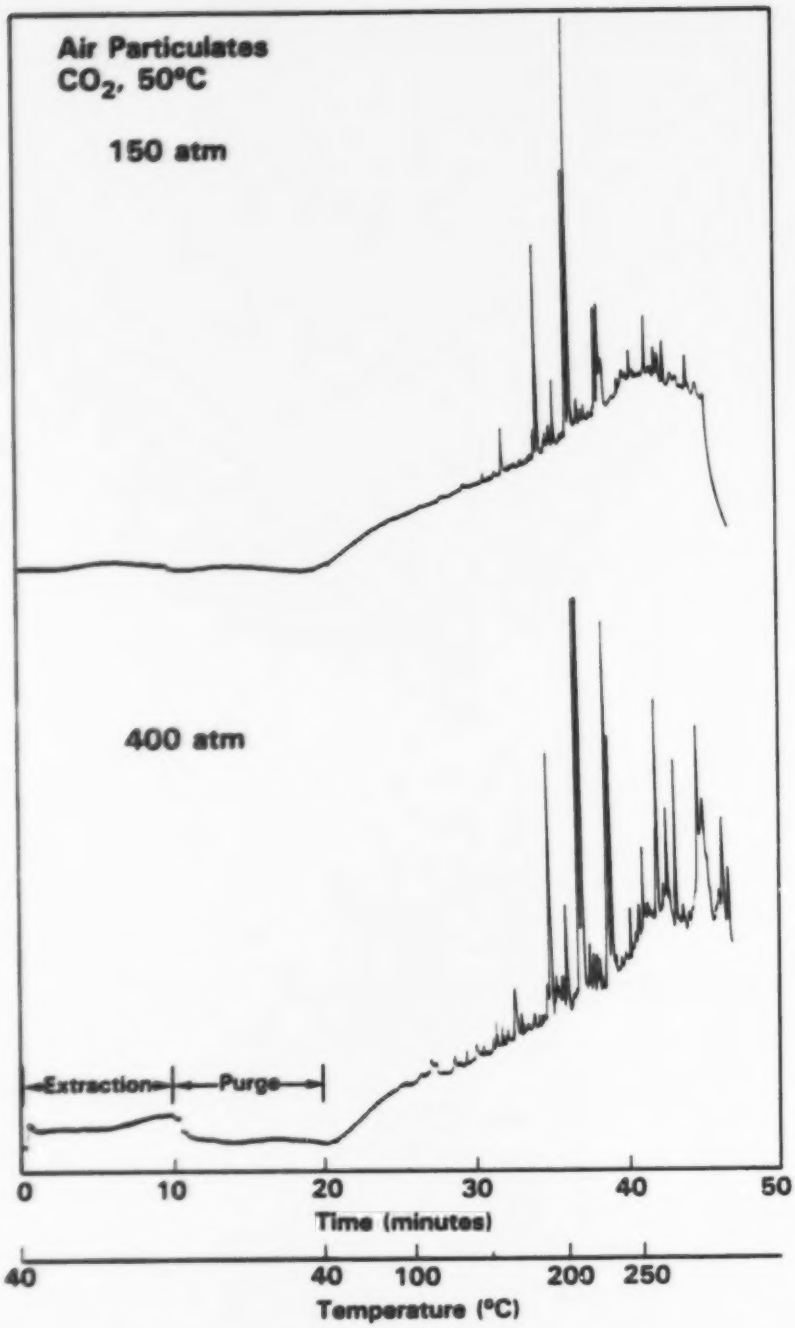

Figure 23. Supercritical fluid extraction-gas chromatography of NBS Urban Dust at two pressures. Conditions: 10 min. extractions at 50°C, 10 min. purge, temperature programmed from 40 to 250°C at 10°C/min., 15m x 0.25 mm fused silica column coated with SE-54.

ted. If more exhaustive extractions had been performed, much sharper fractions could have been obtained. However, since very little material is required for on-line extraction-analysis, very long extraction times or several multiple extractions would have been required for the sample to have been selectively exhausted. One approach to obtain a more exhaustive extraction is to have a larger flow volume through the external collection restrictor (relative to the on-column process) and allow the extraction to proceed during the gas chromatographic analysis. Additional extraction time at lower pressures before extracting at higher pressures could also be utilized. The low quantities of analyte needed for on-line extraction-analysis also offers distinct advantages. For trace quantities of material that would be lost or contaminated during conventional work-up procedures this methodology provides a viable approach. In summary, on-line supercritical fluid extraction-gas chromatography provides a method of selectively extracting complex matrices and obtaining high-resolution capillary gas chromatographic separations.

FLUORESCENCE DETECTION SUPERCRITICAL FLUID CHROMATOGRAPHY

The favorable properties of supercritical fluid mobile phases (11) result in enhanced chromatographic efficiencies per unit time relative to liquid chromatography and enhanced capability for the separation of materials of lower volatility relative to gas chromatography. Carbon dioxide has been used extensively as a mobile phase in capillary supercritical fluid chromatography due to its mild critical parameters, chemical inertness, and compatibility with flame ionization detection. However, the chemical properties (e.g. solvent power, specific solute interactions, etc.) of other fluids would also be desirable, especially for larger and more polar molecules that exhibit limited solubility in carbon dioxide. Such fluid systems, including pure compounds and binary fluid mixtures, are not generally compatible with flame ionization detection (i.e., the fluid gives a significant detector response). Consequently, alternative detection methods must be considered. One method that provides extremely high sensitivity (important in capillary SFC applications due to low analyte concentrations) and is instrumentally straightforward is fluorescence detection.

As discussed in the experimental section of this report, the adaptation of a commercial HPLC fluorescence detector for capillary SFC required replacing the existing flow cell with a length of small-diameter fused silica tubing to allow on-column detection. A number of problems occurred and were overcome in this process. In addition to the expected modifications to allow routing of the fused silica tubing, very tight constraints were found to be necessary for the placement of the cell. Perfect alignment of the excitation light with the center of the 0.25mm i.d. tubing (x-axis) and with the center of the window on the tubing (y-axis) was required. The proper placement of the exit end of the analytical column immediately below the light path in the window tubing also required special attention. To prevent unacceptable levels of scattered background light from diffraction on the silica walls, narrow slits were used to collimate the light beam in the interior of the cell. Various sizes of on-column window tubing were evaluated. Smaller cells provided lower sensitivities due to the shorter path lengths and larger cells contributed to significant detector band-broadening. The 0.25mm i.d. tubing provided maximum sensitivity without substantially increasing the band-broadening. It was also easier to illuminate the interior of the cells by using the larger 0.25 mm i.d. tubing. The effective volume of the on-column flow cell using this tubing was approximately 0.25 µl.

An example of a typical chromatogram obtained using the fluorescence detection SFC instrumentation is shown in Figure 24. This separation of a model compound mixture was obtained using supercritical pentane at 210°C as the mobile phase and a short 5m x 50 µm i.d. fused silica capillary column. An excitation wavelength of 254 nm was used with collection and detection of the entire emission spectrum. The analyte components were eluted by increasing the solvent power of the mobile phase by programming the pressure from 400 to 735 psig at 10 psi/minute. The benzene solvent peak was easily detected at the excitation wavelength used. Sharp narrow peaks were obtained, with all the components in the mixture being easily resolved in less than thirty minutes. Very high sensitivity was also achieved as evidenced by the high signal-to-noise ratio with less than a nanogram of each component being injected. A chromatogram of the same mixture obtained under the same conditions as the separation shown in Figure 24, except for the excitation wave-

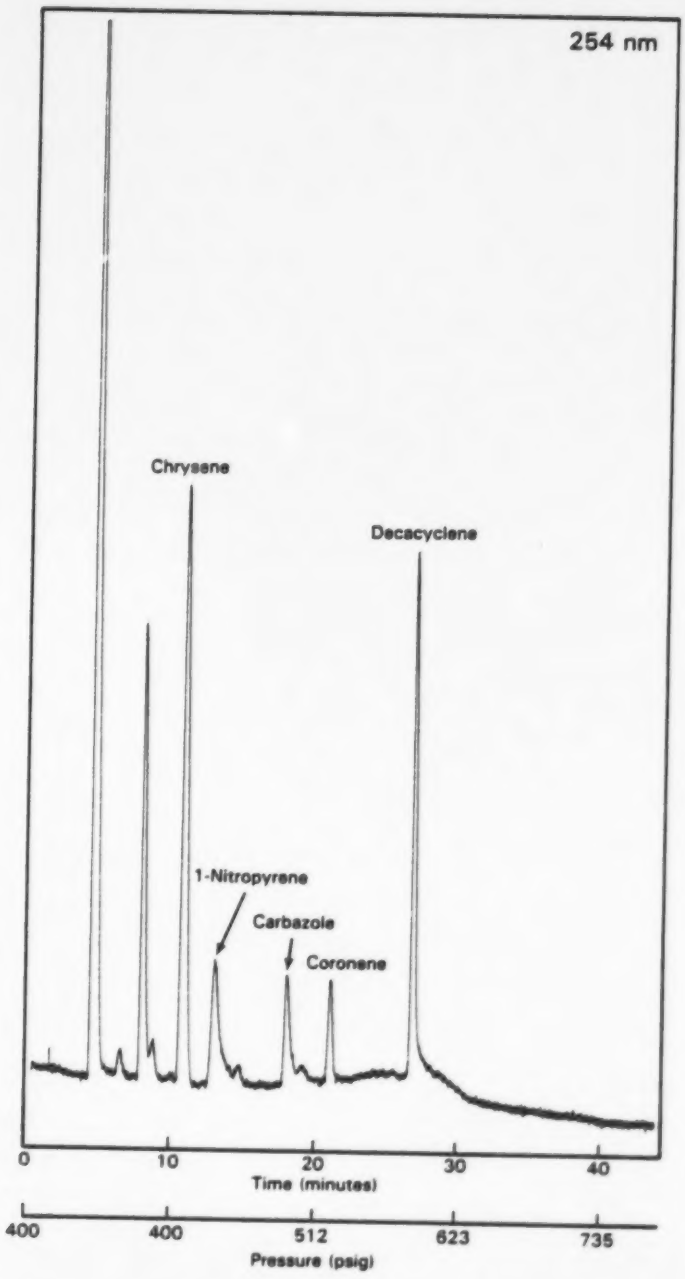

Figure 24. Capillary supercritical fluid chromatogram of the model compound mixture using fluorescence detection with excitation at 254 nm. Conditions: 5m x 50 μm deactivated fused silica column coated with a highly crosslinked SE-54 (5% phenyl polymethylphenylsiloxane) stationary phase, supercritical pentane at 210°C and 400 psig, pressure programmed after 10 min. at 10 psig/min to 735 psig.

length being changed to 270 nm, is shown in Figure 25. It is interesting to note the changes in relative peak heights of the components from one excitation wavelength to another. The chrysene obviously has a much higher fluorescence efficiency at 270 nm than 254 nm. This example points out the selectivity that can be achieved with fluorescence detection. It also points out the necessity of calibrating each component of interest in a quantitative analysis as the response factors can differ drastically for each compound.

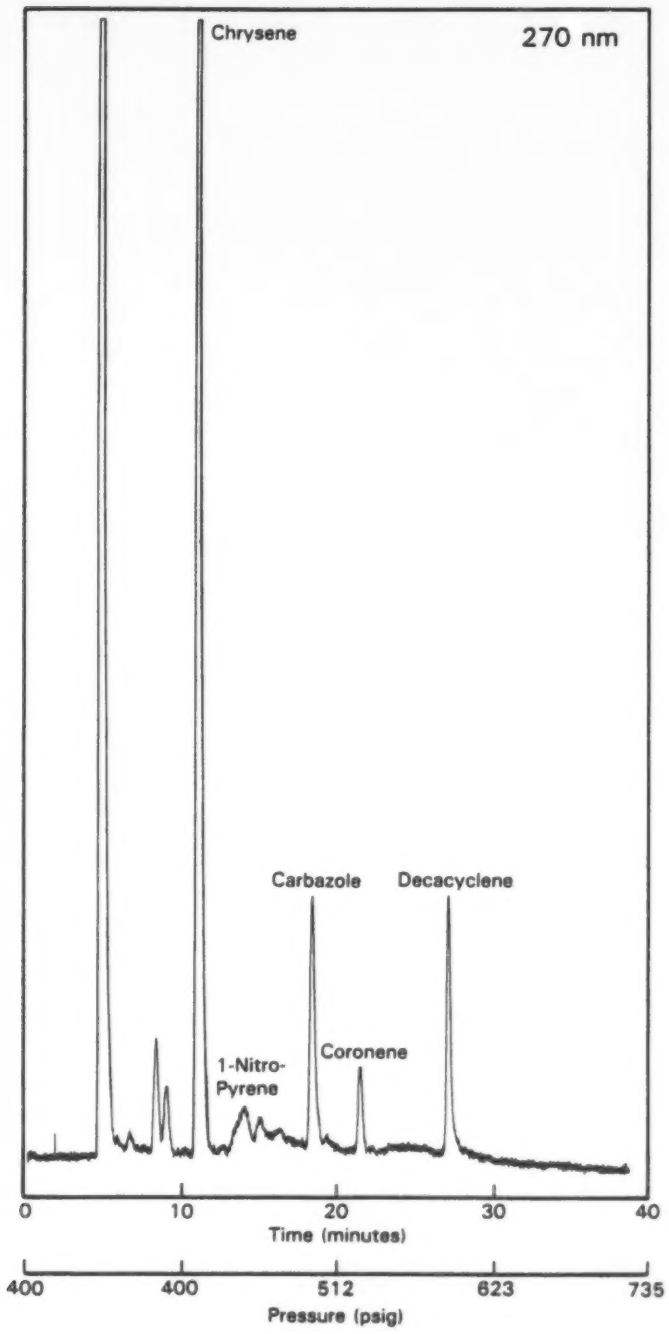

Figure 25. Capillary supercritical fluid chromatogram of the model compound mixture using fluorescence detection with excitation at 270 nm. Conditions the same as in Figure 24.

REFERENCES

1. Schneider, G. M., E. Stahl and G. Wilke, Eds. Extraction with Supercritical Gases. Verlag Chemie, Deerfield Beach, FL, 1980.

2. Wassen, u.Van, I. Swaid and G. M. Schneider. Physicochemical Principles and Applications of Supercritical Fluid Chromatography. Angew. Chem. Int. Ed. Eng., 19, 575-587 (1980).

3. H. M. Spencer. Laboratory Methods for Maintaining Constant Humidity. In: International Critical Tables, E. W. Washburn, Ed. Vol. I, McGraw-Hill, New York, NY, pp. 67-68, 1926.

4. Smith, R. D. and H. R. Udseth. Direct Analysis of Supercritical Fluid Extraction Products. Sep. Sci. Technol., 18, 245-252 (1983).

5. Smith, R. D. and H. R. Udseth. A Method for the Direct Analysis of Supercritical Fluid Coal Extraction and Liquefaction. Fuel, 62, 466-469 (1983).

6. Peaden, P. A., J. C. Fjeldsted, M. L. Lee, M. Novotny and S. R. Springston. Instrumental Aspects of Capillary Supercritical Fluid Chromatography. Anal. Chem., 54, 1090-1093 (1982).

7. Wright, B. W. and R. D. Smith. Application of Capillary Supercritical Fluid Chromatography to the Analysis of a Middle Distillate Fuel. Chromatographia, 18, 542-545 (1984).

8. Wright, B. W., P. A. Peaden, M. L. Lee and T. J. Stark. Free Radical Crosslinking in the Preparation of Non-extractable Stationary Phases for Capillary Gas Chromatography. J. Chromatogr., 248, 17-34 (1982).

9. Brunner, E. Fluid Mixtures at High Pressures; I. Phase Separation and Critical Phenomena of 10 Binary Mixtures of A Gas + Methanol. J. Chem. Thermodyn., 17, 671-679 (1985).

10. Reid, R. C., J. M. Prausnitz and T. K. Sherwood. The Properties of Gases and Liquids, 3rd ed, McGraw-Hill, New York, NY, 1977, Chpt. 5.7.

11. Gouw, T. H. and R. E. Jentoft. Practical Aspects in Supercritical Fluid Chromatography. Adv. Chromatogr., 13, 1-40 (1975).